

# **THE STORY OF CHEMISTRY**

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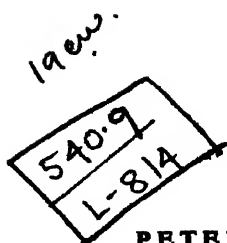
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## PART ONE

### INTRODUCTION

Chemistry is among the youngest of the natural sciences. Mathematics, physics and astronomy have a history of several thousand years, as witnessed by the still famous names of Thales, Pythagoras, Euclid, Archimedes, Aristarchus, Ptolemy, etc. The efforts that finally led to the creation of chemistry were for a long time misdirected. Other sciences, e.g., medicine and jurisprudence, had from the very beginning a clearly defined purpose, even if the ways leading to that purpose changed so frequently in the course of the centuries. But the activities from which chemistry developed were long carried on aimlessly and planlessly, or else they served other purposes. It was only quite late in the day that men became aware that the real task of chemistry is to study the properties of different substances and their mutual transformations. This happened in the 17th century, when chemistry became a genuine and independent science. From then on it can claim a history of its own.

But anybody who would follow up the history of chemistry for only 300 years would have no understanding of the prevailing views and of the condition of natural sciences at that time. He would also find it very difficult to follow their later development. The prehistory of chemistry reflects, more than any other science, cultural history generally. The apparent frills and complexities that mark the growth of the human spirit are especially prominent in chemistry. To understand them one has to delve into the ways and means of arriving at

views that seem to us weird and almost inconceivable. And one must also be able to follow the march of knowledge, with all its twistings and turnings, until it finally swings onto the broad highway that leads to a true science.

Some may feel that history is not the right pursuit for a student of chemistry and of the physical sciences in general. He deals, after all, with natural data that are in themselves unhistorical. The properties of substances are the same now as thousands of years ago. But science always embodies only the actual state of knowledge of these natural data at any given time. The course of time produces not only an increase in the number of individual facts but also occasional fundamental changes of general scientific views and basic assumptions. The physical scientist must realize that the present state of his particular discipline is not permanent, that everything is in flux and that today is but a bridge between yesterday and tomorrow. It is only thus that he can understand the present. Only an eye sharpened by looking at the course of history can view today's ideas and concepts critically and estimate them at their true value. As Goethe put it: "The history of a science is the science itself." A physical scientist who considers his discipline in the light of history does not therefore engage in amateurish pursuits but rather does something necessary for the understanding of his work.

### *The name "chemistry"*

This name requires an explanation. What is its origin? It is first used by the Alexandrian scientist Zosimus from Panopolis (Chemnis) in Egypt in the 3rd century B.C.

"Chemi" is the old name of Egypt. The Greek term "che-meia" (to be supplemented by "techne") was therefore said to mean "Egyptian science," practiced by Egyptian priests in their temples and also called "hagia techne," holy science.

But there are two other possible etymologies.

Edmund O. Von Lippmann, the historian of chemistry, deduces its name from the Egyptian word "chame" or "kame," meaning black and referring in the first place to the black soil of the Nile Valley. "Chemistry" would thus mean the "black art" which indeed it was throughout the middle ages.

But the most likely etymology is that proposed by the classical philologist Hermann Diels and stressed by Julius Ruska. The word "chymeia" was often used side by side with "chymeia." It comes from the Greek "chyma" meaning casting. The word "chymia" would thus mean the technique of casting metals. The middle ages added to it the Arabic prefix "Al" and got "alchymia," the word used to describe experiments in the artificial transformation of metals practiced then and well into our time. (They were also called simply "chrysopoia," the making of gold.) The "y" of "chymia" became "e" in German—hence "Chemie" and "Alchemie"—and "i" in French (chimie) and Italian (chimica).

### *Survey of Historical Divisions*

Our civilization stems from the ancient cultures of the Mediterranean. Egyptians, Babylonians, Persians, Greeks and Romans created the foundations on which European science was built. And so we start our history with the time when these ancient cultures reached their peak. This history could be sub-divided into certain periods that have individual characteristics. Certain basic ideas appear, vary with the general condition of culture, and bring about a new period of development. The transition is gradual: there are always precursors and epigones. The periods may not be clearly delimited but they are clearly distinguished.

I. *The Period of Prehistory* (Antiquity till 4th century B.C.). Knowledge and ideas of ancient Mediterranean peo-

ples, especially the Greeks and Romans.

II. *The Period of Alchemy* (Middle ages from 4th till beginning of 16th century). Origin in the Hellenistic culture of Egypt; taken over by the conquering Arabs in the 7th century and transferred to Spain and Italy. Further spread of alchemy to the Christian West at the beginning of the 13th century. Task and purpose: transformation of metals (manufacture of gold) and discovery of a panacea and magical ferment, the "grand elixir," "magisterium" or "philosopher's stone." Intricate writing and mystery monging, gradual decline into phantasy, epigones as late as the 19th century.

III. *Period of Iatrochemistry* (Beginning of 16th to middle of 17th century). Paracelsus puts chemistry in the service of medicine. He gives it as tasks the chemical interpretation of the phenomena of life and the application of various chemical compounds, especially the metallic salts, as medicines ("ar-cana") against diseases, instead of searching for the panacea of the alchemists. His successors were partly common quacks and partly serious investigators. Simultaneous development of chemical techniques by Agricola.

IV. *Period of Independent Chemistry* (since middle of 17th century). Brought about by the German Jungius and the Englishman Boyle. Recognition that the real task of chemistry is the study of the properties of various substances and their mutual transformations. The phlogiston theory of Becher and Stahl soon dominates all chemistry. Clarification of the concept of element but quite unclear concepts of mass and weight. Qualitative age.

Lavoisier develops a new oxidation theory (1777-1789) from the discovery of oxygen by Scheele (1771) and Priestley (1774). He also clears up the concepts of mass and weight of chemical substances and, as a physicist, founds the age of qualitative chemistry. Stoichiochemistry is founded by J. B. Richter (1792) and a new atomic theory by Dalton (1803);

various fundamental laws are established. Chemistry further developed, especially under Berzelius. Woehler's synthetic manufacture of urea (1828) inaugurates organic and synthetic chemistry. Liebig's great importance as investigator and teacher. Individual fields of study develop and foster each other's growth. Clarification of theoretical concepts and ideas. Growth of physical chemistry, in Germany under the leadership of Bunsen. Ever more rapid development of new scientific disciplines, sometimes creating fundamental changes (e.g. radioactivity), into our day.



## I. PERIOD OF PREHISTORY (Antiquity till 4th century B.C.)

Chemistry as we understand it today was unknown to antiquity. Man learned individual chemical facts through his day-to-day experience and his economic activities; but there was no planned research. The Greeks and Romans took over in part the experience in natural sciences gathered by the ancient Egyptians, Babylonians, Assyrians, Phoenicians, Medes and Persians; but they did not substantially enrich that experience. The cultured Greeks generally believed with Aristotle that work produces a low mentality; but the results of their purely intellectual activities were all the more brilliant. Our culture and our science are still based on the thoughts and the investigations of the Greek philosophers.

### 1. *Historical sources*

Archeology has produced a number of data about the state of knowledge and techniques among the peoples of antiquity. This applies especially to Egypt, where the excavations of the royal tombs revealed some very surprising finds. Individual writings that have been preserved form another source of information. Among the most important is the "Ebers Papyrus," discovered in 1872 at Thebes by the Egyptologist Georg Ebers and now at the Leipzig University Library. This excellently preserved papyrus dates from about 1600 B.C.; its contents are mainly pharmaceutical and medical. Another is

the "Papyrus Brugsch major," found near Memphis in 1826 and now in Berlin, dating from the time of Rameses II (second half of the 14th century B.C.). The Old Testament yields copious information about the state of scientific knowledge among the Jews.

The following Greco-Roman writings should be considered: Homer's "Iliad" and "Odyssey" (10th century B.C.), Plato's "Timaeus" (5th century B. C.) and Aristotle's "On Heaven" and "On Growth and Disappearance" (4th century B. C.). Theophrastus, an important pupil of both these philosophers wrote a special book "On Minerals," a handbook of natural science containing the first known mentions of mineral coal, cinnabar, sulphide of arsenic, etc. Of the Romans, the Elder Pliny, who died in the Vesuvius eruption of 79 A. D., summarized the knowledge of natural sciences of his time in the 37 books of his "Natural History." The Greek Dioscorides, living about the same time as a Roman military physician in Asia Minor, gives a detailed picture of contemporary medical and chemical knowledge in his great collection "Materia Medica." The writings of the famous physician Galenus of Pergamum (second half of the 2nd century A. D.), some of which are spurious, offer numerous data on the physical sciences.

The two papyri now known as "Leydensis" and "Holmensis" from their respective locations at Leyden and Stockholm were found in 1828 in the cemeteries of Thebes and date from the 3rd century A. D. They give and explain techniques of working metals, making artificial jewels, pearls and other ornaments, and the dyeing of woollens with various dyes. These and other trades were practiced in Egyptian temple worships, partly in secret. From about the same time date the writings of Zosimus of Panopolis, already mentioned.

## *2. Knowledge of Chemistry in Antiquity*

Among many peoples culture and education were from the very beginning connected with religion. The priests were also teachers and educators of their people, they created and fostered the spiritual forces and were the true bearers of culture. In Egypt particularly science as well as religion was cultivated in the temples and native and foreign seekers after knowledge made their way to them. Greek philosophers and statesmen like Solon, Pythagoras, Democritus and even Plato went to them to enrich their knowledge.

Practical activities increased knowledge of the physical sciences from very early days. This applies especially to the working of metals, pottery, the manufacture of glass, dyeing, the brewing of beer, the preparation of medicines and the extraction of vegetable poisons. Medicine was at first naturally practiced by the priests.

The extraction of metals from natural ores and their further treatment is the first stage leading to a higher civilization. The word "to metallon" appears already in Herodotus (5th century B.C.), where it means "mined." Pliny (1st century A.D.) derives the word from the Greek words "met'alla," one after the other, from the strata found in mining galleries. But more likely the etymology is Semitic: "matal" means to forge in Hebrew, and an Arabic derivation is also a possibility. The first metals to be worked were, as was only to be expected, those that appear naturally in a pure state: copper and the precious metals gold and silver.

The Old Testament and other ancient writings speak of a legendary land of gold called "Ophir"; Nubia, which lies South of Egypt, was also praised for its abundance of gold. The discovery of the Egyptian royal tombs, especially the recent one of Tutankhamen, showed how lavishly gold was used for the worship of the dead. Herodotus reports the fabu-

lous gold treasures of the Lydian kings Gyges and Croesus (8th and 7th centuries B. C.). Gold and silver alloys, both natural and artificially melted together, were also known.

Such alloys, e.g., of three or four parts of gold with one part of silver, were called in Greek "ho elektros" (to be distinguished from "to elektron" meaning amber). But it was not known how to separate the metals after they had been alloyed since the aqua regia was not available.

The famous scientist Archimedes (3rd century B. C.), asked by King Hiero II of Syracuse to determine the gold content of his crown, solved this difficult problem by determining the specific weight and shouted triumphantly "Heureka"—I have found it.

Copper, which appears in pure state, was already known in the fourth millennium B.C. in Egypt, Babylonia and Asia Minor. The main sources were the Sinai peninsula, the island of Cyprus and Spain. The stones of the oldest pyramids still show the marks of copper tools like stone saws. The Greek word "chalkos" means both copper and its alloys, especially bronze. The Latin word "cuprum" is derived from "aes cyprium," the Cyprian ore. Pliny already mentions copper salts, e.g., blue vitriol.

Next to copper, tin was important from early times. It was found in Spain and later in Britain (Cornwall) as cassiterite, and also as a mixed copper and tin ore. The copper-tin alloy was known in Egypt around 3000 B. C.; in the West it made the bronze age follow the stone age around 2500 B.C. Because of its greater hardness bronze was used for cutting tools and weapons, including those carried by Homer's heroes in the Trojan War (about the 12th century B. C.). Our word "bronze" comes from the Latin "aes brundisium" or "brundisium," the ore from Brindisi, the town in Southern Italy where bronze industry flourished. Its excellent metal mirrors were famous.

Zinc became known as a pure metal only quite late—in the 16th century A. D. But by adding siliceous calamine to melting copper a yellow alloy known as “brass” was obtained much earlier and used for various purposes. Its German name “Messing” comes from the fabulous people of Moissinoikoi who were its great users according to Aristotle.

Lead, which mostly appears in its natural state together with silver, was early separated from it by fire heat in the refining furnace. Greeks and Romans used it in various forms: litharge, white lead, minium and pure metal (known as “black tin” to distinguish it from “white tin,” i.e., tin). Herodotus reports that the Greeks used to coat their ships with minium. The Romans used metallic lead for various vessels and also for water pipes. They were aware of its poisonous effects.

Mercury was first mentioned by Theophrastus (about 300 B. C.). It was extracted from natural cinnabar by treating it with copper or iron with addition of vinegar and was called “hydrargyros,” liquid silver (from “hydor,” water and “argyros,” silver). Pliny distinguishes between mercury obtained industrially and that found in its pure metallic state, especially in Spain. He also describes a method of purifying it by pressing it through leather (Dioscorides describes its purification by distillation). Mercury was also used for alloys, e.g., with gold.

Iron does indeed widely appear in nature in the form of various compounds. But its conversion into metal requires special techniques which were laboriously discovered in the course of centuries, if not millennia. True, iron smelting furnaces dating from 3000 B. C. were found in Egypt. But the production of metallic iron became known in Europe very much later; the Iron Age followed the Bronze Age only around 500 B. C. This is also true of the hardening of iron into steel: known to the Egyptians, the technique was only gradually developed by other peoples. The Romans got their

steel weapons mostly from Styria and Carinthia. Pliny mentions the magnetization of steel by the application of magnetite, which got its name from the city of Magnesia in Asia Minor, its main source.

The seven metals mentioned here—gold, silver, copper, tin, lead, mercury and iron—are the only ones known to antiquity and also to the middle ages. They represent about one tenth of the existing metals. These seven metals were regarded as symbols of the seven heavenly bodies, i.e., sun, moon and five planets. Since seven happened to be one of the holy numbers, this made it difficult to classify newly discovered elements as metals in the beginning of the modern era.

The manufacture of pottery is one of the first signs marking the emergence of a higher civilization: the form and ornamentation of excavated pottery vessels are used to determine the cultural stage reached by a people. In Italy, the potter's craft flourished especially in Arretium, now Arezzo in Tuscany. The glaze of the pottery made there from red "terra sigillata" was proved to contain boric acid. Among the Chinese, whose civilization dates from the third millennium B. C., pottery was early refined into porcelain. Both Egyptians and Chinese were quite early engaged in the manufacture of glass, probably derived from observing the process of melting out quartz sand containing gold with lime, soda and potash. While old Egyptian glass is opaque and colored more or less darkly, excavations at Tell el Amarna yielded quite transparent and colorless glass dating from the 15th century B. C. Elsewhere, there were numerous finds of artificially colored glass and enamel, e.g., blue glass containing copper or cobalt like the lapis lazuli of Nippur dating from about 1500 B. C. On the other hand, blown glass can be dated only from the age of Augustus, under whom Alexandrine craftsmen introduced it to Rome. From there it spread to Roman provinces like Spain, Gaul and West Ger-

many. The German towns of Cologne, Worms and Trier had a glass industry of their own by the first century A. D.

Lime used in the preparation of cement was early obtained by burning natural limestone. In addition to the common salt obtained since time immemorial from the sea or from saline springs, there was soda (known in Egypt, where it appears in natural state as "t'hrona") and potash, obtained as residue from burning wood. To this very day, salt is produced in China and elsewhere in the East from "salt gardens" by evaporating sea water in the sun. Another primitive technique consists in pouring salt water on burning wood.

Recent research has proved that salt was, together with the dry climate, a most important factor in the art of mummification which reached such a high state in Egypt that the mummies of pharaohs have survived unchanged for thousands of years. The bodies, from which soft parts like brains and intestines were removed, were placed for several weeks or even months in a salt bath—they were, indeed, "pickled." The mummies proved to contain no trace of soda or salt-peter. The bodies were then dried in the air, coated with ochre and gum mucilage and treated with various resins and spices, procedures also designed to prevent the entry of destructive micro-organisms. Alabaster vessels dating from 3000 B.C. and found in rock graves near the pyramid of Cheops contained a perfectly preserved 3% caustic soda solution.

Salt-peter was also known to antiquity. The Greek "to nitron" and the Latin "nitrum" can mean soda, caustic soda or common salt. Salt-peter was later called "sal nitri." The Chinese used it very early in the preparation of fireworks that were the precursors of gunpowder. Alum, which appears in natural state, was used for tanning and other purposes. Herodotus reports that after the Temple of Delphi burned down the wood used for the new building was soaked with

alum as a fire preventive (6th century B. C.). Various mineral salts were used for specific purposes, e.g., copper vitriol by Roman cobblers to blacken leather. Both Pliny and Dioscorides mention its emetic effects.

Sulfur was, with carbon and the seven metals, the only element known as such to antiquity and the middle ages. Burning sulfur is used for fumigation already in Homer. In the middle ages, mercury and sometimes arsenic were counted with sulfur as basic elements that replaced or supplemented the four basic elements of antiquity.

Dyeing is among the earliest industries. Clothes were mostly dyed with animal and vegetable dyes. Madder, indigo, litmus, wood and other plants yielded useful dyes. The costly juice of the purple snail was reserved for the royal mantle. The mineral dyes used included white lead, minium, lazulite, smalt, verdigris, iron ochre, cinnabar, orpiment and realgar. Finely ground antimonite ("Stimmi") yielded the dark face paint of Egyptian beauties, whose toilet articles could well stand up to modern requirements.

Ointments and perfumes were obtained from animal and vegetable fats. Lanoline was known in addition to oil of turpentine and numerous volatile oils: it is mentioned by Pliny. Starch obtained from wheat grains was known, too. But neither the Egyptians nor Greeks nor Romans knew soap. Strangely enough, it was the Gauls and Teutons who introduced soap to Rome.

The beginnings of beer brewing can be traced very far back. The Egyptians knew beer thousands of years ago and some beer is still prepared there today by the method described by Zosimus. Brewing was also eagerly practiced by other peoples like Gauls and Teutons. The "kvass" which several Slavonic peoples prepare today from various kinds of grain is said to have been the beer of antiquity. The making of wine from grape juice is probably even older than



brewing of beer. It is enough to recall the Biblical story of Noah. Since sour fermentation appeared in the process in addition to alcoholic fermentation, vinegar belongs to the industrial products produced in early antiquity. It also remained the only acid known to antiquity and the middle ages until the 13th century. Hannibal is said to have exploded big rocks with it when he crossed the Alps with his elephants. He probably did it by heating the stones with huge wood fires and then pouring on them cold water mixed with vinegar. This produced cracks in the rock which could then be worked with iron tools. Cleopatra dissolved her most precious pearl in vinegar and drank the solution.

The medicines used in antiquity were mostly made of animal and vegetable substances. But the Egyptians also kept such chemical preparations as soda saltpeter, alum, verdigris, litharge and orpiment in wooden boxes or glass and pottery vessels that graced the priestly apartments. They also knew how to prepare various pills, ointments, plasters and salves. Nor did they lack special purgatives against spool worms and tape worms. The Berlin Museum has a medicine chest dating from the 11th dynasty (about 2000 B.C.) and containing all kinds of medicines.

Medicines became so numerous that Pliny did not want to enumerate them all. Later on, the medicines prepared by the Greco-Roman physician Galenus (2nd century A. D.) became very important. Among them is "Theriac," which was originally prepared by King Mithridates (1st century B. C.) and Andronicus, Nero's personal physician. Theriac is a mixture made from several dozen ingredients; it was used throughout the middle ages and well into modern times—it is still mentioned in the first German pharmacopeia, dated 1874. Special vegetable extracts were used as magic potions and poisons ("good poisons," "bad poisons" and "killers"). It is enough to recall here Socrates' cup of hemlock. The

medieval executioners used all kinds of narcotics to ease the last moments of witches and other victims that medieval justice condemned to the stake.

### 3. *Theories of Greek philosophers*

The practical knowledge of the ancients, which was pretty scanty by our lights, is far less important for us today than their theoretical views. This applies in the first place to the people that taught philosophy to the world. The Greeks had little enough aptitude for experimental science; but their capacity for pure logical thinking was all the more brilliant. They are the actual founders of philosophy and they thought out the basic philosophic problems not only for themselves but also for the succeeding generations. Our own civilization and intellectual framework are still based on Greek philosophy.

The first fundamental question to agitate thinking men was that of the primary substance. They asked: What is the world composed of? They felt that the correct answer would solve all the riddles of our existence and of the natural phenomena. This was the task that the Ionian philosophers set for themselves.

Thales of Milet, about 600 B.C., stands at the gate of the mighty temple of Greek philosophy. He was a contemporary of King Kroesus and the lawgiver Solon. To men living in the isles of Greece, the infinite sea carrying the earth disk seemed to be the prime cause of all existence and the original mother of all living beings. And so Thales proclaimed water to be the primary substance ("he physis") of all things. He said "Ariston to hydor"—the noblest (best) is water. Everything comes from water and everything goes back to it. His pupil Anaximander replaced water by an eternal infinite ("apeiron") and unlimited ("aoriston") as the original and primary substance ("arche"). Anaximander's pupil Anaxi-

menes proclaimed air ("pneuma") to be the real basic substance. All individual beings were created from its condensations.

Other philosophic heads concerned themselves with the problem of the basic form and of the general world order. Pythagoras of Samos (late 6th century B.C.) completed his studies by travels—he visited the Egyptian priests—and became immortal by his mathematical theorem of the rectangular triangle. He saw number ("ho arithmos") as the original formative force of all things. Only number creates order and harmony, through which a chaotic universe becomes an ordered cosmos (a word he was the first to use).

The latest views on the arrangement of the electrons in the structure of the atom are a pressing argument in favor of Pythagoras' opinion.

The combination of the two questions about the basic substance and the basic form produced the real basic problem of Greek philosophy, that it was able to solve only when it reached its classical peak. The problem is: How does matter acquire form? How are the things of this world created? How can the continuous growth and disappearance, the eternal change, be explained? The succeeding philosophers busied themselves with the third question, that concerning the creation and course of the world. Strictly speaking, there are only two answers to this question. And both of them were thought out by the Greek philosophers to the bitter end.

The Eleatic school was founded by Xenophanes of Elea in Southern Italy (about 500 B.C.) and was later represented by Parmenides, who wrote the epic poem "On nature" ("peri physeos"), Zeno and Melissos (5th century B.C.). They represented the view that there is only one unchangeable being ("to on"), the alone ("hen kai pan") that remains as it is. Everything else is illusion. A change in the being and so the growth and disappearance of things are impossible

because a thing cannot exist and not exist at the same time. Our concept of constant change, obtained by the observation of sense, is logically unexplainable and therefore must be incorrect. It is an illusion of the senses. There is no bridge from the absolute being to the sensually conceived concrete being. The contradiction between natural views and absolute theoretical thought is shown here at its sharpest.

The opposite view, the second possible answer to the difficult question, was represented by Heraclitus of Ephesus (about 500 B.C.), who was called the "dark" or the "weeping philosopher." He held that the change perceived by us is indeed a contradiction in itself but it is a necessary contradiction. The course of the world is indeed unexplainable but it is an original fact. Everything is in a flux—"panta rhei." Fire ("to pyr"), the constantly growing and disappearing flame, is the symbol of the primeval being. Becoming and change are the unity of being and non-being. Divine reason ("to logos"), the primeval fire, maintains the world.

These two opposite views appear to be contradictory and completely mutually exclusive antitheses that cannot be reconciled. And yet a solution had to be sought that would be just to both of them and might possibly combine them in a higher unity. This was possible only by conceiving being not as a single but as a multiple, by assuming a multiplicity of primary substances that remain indeed unchangeable in themselves but produce the apparent growth and disappearance and the constant change by their combination and division and by their mutual influence. This solution to the difficult problem by which the course of the world was interpreted as a mechanical process was again reached in two ways: by the theory of elements and the theory of atoms.

The theory of the elements was originally developed from the contemplation of the starry sky. It is founded on the Babylonian concept that everything earthly is but a reflection of

the celestial. It was developed about 450 B.C. by Empedocles the philosopher who finally threw himself into the Aethna because he was tired of life or because he was unable to still his thirst for knowledge. Four elements of which the world is composed—fire, air, water and earth—correspond to the four planets in the sky. The two basic forces—love (“*philia*”) and hate (“*neikos*”) unite and divide them mutually, which produces the constant change. The actual Latin word “element” dates only from the days of Cicero and was coined from “LMN,” the three central letters of the Latin alphabet; the Greeks used the word “*stoicheion*.” The four elements, which mean less the actual substances than the characteristic properties adhering to them, have played an important part well into the modern era. It was only in the 17th century that natural science developed a true concept of the element.

The other attempt to solve the difficult dilemma proved even more successful. It had a variable fate through the centuries but its basic postulate was proved in our own time to be generally and unconditionally valid. This is the atomic theory, founded by two philosophers living in the late 5th century B.C., Leucippus and Democritus from Abdera in Asia Minor. The latter, called in contrast to Heraclitus “the laughing philosopher” is considered to be more important. Like Pythagoras he is said to have frequented the Egyptian temple schools. The basic idea is the following: Substances consist of very small units which cannot be perceived by the senses (“*aorata*”) and cannot be further subdivided (“*atoma*”). These “atoms” in empty space are the “being in the non-being” and differ only in size and shape. Whirring in empty space, they collide and separate again, governed only by the law of nature. blind necessity (“*anagke*”). There are no accidents or arbitrary happenings, everything is necessary. Spirit and fire, too, consist of atoms that are especially fine and smooth. Scientific materialism was founded with this

view.

Anaxagoras from Clazomene in Asia Minor represented a somewhat different view. Like Empedocles, Leucippus and Democritus he denied actual growth and disappearance, and he, too, viewed all happenings as mixture and untangling of indivisible particles. But his atoms are qualitatively different. They are the primary seeds of all things ("spermata panton chrematon"), later called "homoioreia" by Aristotle. They are not governed by blind natural law; but divine reason ("ho nous") creates the ordered cosmos from the unordered chaos of the original state. Anaxagoras is the first outspoken dualist: he combines the basic thoughts of his predecessors into a totality. He closes the realistic period of Greek philosophy.

A century and a half later, the atomic theory was represented in Athens by Epicurus (342-270), the "philosopher of happiness." He ascribed to the atoms weight in addition to a definite shape and size. The last adherent of the atomic theory in classical antiquity was the Latin writer Titus Lucretius Carus (98-55), who composed the great didactic poem "On the nature of things" ("De rerum natura").

Greek philosophy had turned away from the investigation of nature in the 5th century and withdrew to purely human problems. This is the age of the Sophists, in which rhetorics flourished but gradually degenerated into empty and witty dialectics. Socrates (469-399) opposed this trend with his search for truth and his recognition of the good, together with his clarification of the concepts. His great pupil Plato (429-347) founded in 387 in the garden of Academos near Athens a philosophical school that became known as the "academic." He rejected the atomic theory; he conceived the world as a reflection of eternal ideas (the theory of ideas) and as a living work of art. In his book "Timaeus" he goes back to the four elements of Empedocles. He conceives them

as consisting of the same primary substance ("hyle") but differing through differently shaped surfaces, consisting of two kinds of rectangular triangles. The four elements have each a different form: fire is a tetrahedron; air an octahedron; water an icositetrahedron, and earth a cube. Like Pythagoras, Plato draws attention to the deep meaning of numbers and of mathematical relations. No one was admitted to his Academy who had not made a thorough study of geometry. Plato proclaimed this science to be the link between idea and reality.

Atomic theory also played no part in the teaching of Plato's pupil Aristotle (381-322) from Stagira in Thrace. He could not admit the assumption of indivisible particles since the division of substances can in principle be carried on indefinitely. Aristotle was the founder of the "peripatetic" school (from "peripatein," to walk about). He thought he could solve all the riddles of the natural phenomena by purely intellectual consideration ("deduction"). He despised the inductive method, for "industrial activity produces a low mentality." Aristotle added to the four elements of Empedocles a fifth, the "ousia" or "aither" or ether, called the "fifth essence" ("quinta essentia," quintessence) by later philosophers. By conceiving the elements not as differing materially but rather as embodiments of differently combined and interchangeable qualities, he founded the concept of the transformation of elements ("transelementation") that became so extraordinarily important later on. There exist four primary qualities ("qualitates primae") of which each two are contraries: wet-dry and hot-cold. Each element has one quality from each pair. Earth is dry and cold; water is wet and cold; fire is dry and hot and air is wet and hot. The other or secondary qualities ("qualitates secundae") are conditioned by the primary qualities. The four elements are thus characterized; each of them can be turned into another by exchanging its

quality for its contrary, while the fifth quality, the ether, hovers over them unchangeably and penetrates all. The following scheme illustrates this:

*The elements of Aristotle*

dry	wet	cold	hot	
earth	water	air	fire	aether
heavy	relatively light		light	weightless
	relatively heavy			
downward		directions of motion upward		circular
		in medium height		

The four elements with their interchangeable qualities can also be represented as follows:

	hot	
fire		air
dry		wet
earth		water
	cold	

This idea of the transformation of elements by the exchange of qualities was the theoretical foundation of the later activities of the alchemists. Aristotle, the "Stagirite," who was unknown to the Christian West in the early middle ages, became the intellectual patron of alchemy after his writings had become available in Latin through their transmission by learned Arabs. He was revered as the absolute authority.



## II. PERIOD OF ALCHEMY

(medieval, from 4th to 16th century)

### 1. *General*

The theoretical knowledge and technical abilities obtained in antiquity through practical activities did not have a straight-line development after the collapse of the ancient world. Classical Greece produced, by many contacts and minglings with the Orient, a new civilization called Hellenistic. Its spiritual center was the city of Alexandria in Egypt, founded in 331 B.C. by Alexander the Great. It is in Egypt that one must seek the origin of the particular investigations and strange activities that are grouped under the name of "Alchemy."

The art of working metals and various minerals, developed in the temple workshops, managed to produce artificial substitutes for many natural substances that were valued for their rarity and costliness. The temple workers were able to color metals and to produce artificial jewels. This "holy art" practiced for the benefit of the gods was especially fostered in the temple of Memphis, whose high priest was the "protector of artists." Even the statues of the gods had in the end to content themselves with artificial substitutes for precious metals and stones. The papyri of Leyden and Stockholm (3rd century A.D.) give numerous descriptions of such procedures.

In addition to this practical experience gained in the course

of centuries there were other influences of various kinds. The views of Greek philosophers mingled with concepts derived from Babylonian and Persian culture. Plato's teaching of the common primary matter gave rise to the idea of the eternal circulation, the "ring of Plato" (*annulus Platoni*) or the "golden chain of Homer" (*catena aurea Homeri*); Aristotle's theory of transformation had similar effects. As earthly happenings were viewed as reflection of the heavenly, so the behavior of metals and ores within the earth or under laboratory treatment was mystically compared with certain processes of life. Even the male and female principles were applied to the world of metals and minerals. Certain practical experiences and observations, e.g. the complete change in the qualities of blends and gravels through glowing or the copper coating acquired by iron tools in mines under the influence of mine water (which contains copper), strengthened the belief that metals could be transformed and ennobled.

The elements of Aristotle and Empedocles, which truly reflected Greek association with nature, were replaced in the "black kitchens" of the alchemists, under Arabic influence, by mercury and sulfur as the basic elements, joined occasionally by arsenic. Certain observations determined, as is only to be expected, the choice of these elements. Mercury amalgamates easily with other metals and can be volatilized again by heating, while the gleaming metallic ores like galena, antimonite and pyrite, develop sulfurous vapors in roasting. Mercury especially embodies, with its weight and gleam, the metallic principle. The "mercury of the philosophers" (*mercurium philosophorum*) is at the same time the representative of the "cold, passive" group of the Greek elements, earth and water, while the "sulfur of the philosophers" (*sulfur philosophorum*) represents the principle of the inflammable, the "hot, active" group, air and fire. Also, mercury and arsenic were viewed as the male principle ("*arsen*" means

man in Greek) and sulfur as the female principle. Their wedding was expected to produce something new. Later on in the middle ages, salt, representing the unflammable and the soluble in water, was added as a basic element.

One of the chief characteristics of alchemistic writing is that old writings are re-written and new writings are issued under the names of well-known older scientists and philosophers or else supplied with fanciful authors' names. Only very recently laborious historical and philological research succeeded in casting some light on the extremely intricate position of the alchemistic writings. This partly applies to the writings, often quoted as authorities by alchemists, and attributed to the Greek philosopher Democritus. Max Wellman proved that these were mainly composed by Bolos, a Hellenistic writer of the Nile Delta in the 2nd century B.C., and re-written in the early centuries of our era in conformity with alchemistic views.

Bolos belonged to the ascetic and mystic order of Neo-Pythagoreans, which spread from Egypt to Syria and Palestine, where the Jewish Essenes may be considered as its offspring. His work "Physika kai mystika" (Physics and Mystics) expresses the teachings of the Persian prophet Ostanes on the mysterious and magic forces of nature, which emanate from animals, plants and minerals. Bolos composed other writings on all kinds of subjects and made them out to be very ancient books of a secret science that he rediscovered. Thus he claimed to have found in the grave of the Jewish magician Dardanos (about the time of Solomon) the books which Dardanos wrote.

The pseudo-Democritic writings offer three various methods of the transformation of metals:

1. Treating the surface of base metals with certain chemicals and coating them with a thin layer of precious metals;
2. Adding a varnish with a gleam of gold or silver;

### 3. Composition of alloys looking like gold or silver.

Later on, various alchemists quoted the authority of Isis, Hermes or Chymes, Zoroaster, Moses and even Jesus. All this is enough to show just what a weird mixture of Egyptian, Persian, Jewish and other influences was required to grow the strange plant of alchemy.

Other alchemical writings have a history not unlike those of Bolos, whose influence can be traced more or less directly in Pliny and later on in the Leyden and Stockholm papyri. Such forgeries, extravagant claims and mystical veilings of the truth as well as a mysterious and unclear language are typical. A great number of magical and alchemical writings dates from the first Christian centuries, and practically nothing is known about their alleged authors. Such is the case of the mythical Jewess Mary, later identified with Miriam the sister of Moses or else described as a princess of Sheba. Her writings give the first descriptions of distilling vessels, consisting already of filling vessel, discharge pipe and receiver. But the water bath, known centuries earlier, is not mentioned in the surviving fragments of her writings. Another writer of that time, Cleopatra, identified by many with the Egyptian queen of that name, wrote, among others, a work on the making of gold called "Chrysopoia." The high priest and philosopher Comaios is supposed to be her teacher. From the 2nd and 3rd centuries A.D. came various apocryphous writings with weird mixtures of Greek, Egyptian, Jewish, Early Christian and Gnostic views. They are partly preserved in extracts or in rewritten passages.

Alchemy, influenced by wars and the general march of culture and peoples, grew in the course of centuries from such multifarious, turbid and complex beginnings. Or rather, since one cannot really speak of its growth, it led a mystical existence in the twilight. It held out to men the fulfillment of their ancient wish dreams. It offered them the chance to win

great treasures by transforming base metals into silver and gold. At the same time it promised them a universal panacea (from the Greek "panakeia") or a great "arcanum" (Latin word for "secret") that would heal all diseases of men and metals and possibly had the gift of bestowing eternal life. The phantom of finding the "magisterium," the "philosopher's stone," the elixir, or whatever its name, kept mankind in its ban for a thousand years. Its seduction was felt well into the modern era.

## 2. *Hellenistic alchemy in Egypt* (middle of 4th till 7th century)

Alexandria, named after its founder, became under the Ptolemaean rule one of the most splendid cities of antiquity. Its lighthouse, 500 feet high, directed incoming ships for 35 miles and was a symbol of its economic and cultural importance for the peoples of the Mediterranean. Splendid palaces, temples, theatres, museums and other buildings as well as the great library adorned this city of millions in which a rich cultural and scientific life grew up. Among the "Alexandrians," the scientists active in the city, we find from the 4th century onwards the chief representatives of alchemy.

Zosimus from the city of Panopolis (in Greek) or Chemnis (in Egyptian) in Upper Egypt is considered to be the first true alchemistic writer. He is said to have taught and written in Alexandria as a Gnostic Christian. He lived about 350-420 and very little is known of his life. His chief work, that made him famous for centuries, was an encyclopedic handbook of the entire scientific knowledge of his time which might also be regarded as the first textbook of alchemy. It is composed in the form of didactic letters to a noble woman, his "mystical sister" Theosobeia, and is preserved only in unconnected Greek, Syriac and Arabic fragments. Another one of his

works, also very incompletely preserved, is called "On Force." It is written in a very dark and enigmatic language and describes strange dreams and visions. Zosimus quotes Hermes and other authorities and calls the holy and divine art of ennobling metals developed by Egyptian priests by the name of "chemeia"—chemistry. He was also the first to develop the teaching of the "great mystery" that was important throughout the alchemistic period. This was the "xerion" that was supposed to act like yeast and, when used as dusting powder, changed large quantities of base metals into gold.

Other alchemistic writers of the 4th century include Pelagius, who wrote "On the divine and holy art" and Synesius, formerly falsely identified with the bishop of Ptolemais of that name. Olympiodorus, who visited in 412 the court of Attila as envoy of the emperor Honorius, wrote in the 5th century. Of later writers Philosophus Christianus and Stephanus (7th century) might be mentioned. The works of these and other writers of that time consist primarily of repeated copyings from older writers.

The highest authority of this Hellenistic-Egyptian age was a mythical personage, the "thrice greatest Hermes," Hermes Trismegistus. He was worshiped as the lord of souls and spirits and the master of all wizards and magicians. He was identified with all kinds of Egyptian and oriental gods, especially with Toth who was a kind of Minister for Culture in the Egyptian Pantheon. The staff with the winding serpent is his symbol. He is supposed to have enshrined his mysterious knowledge in writings, whose number constantly grew. These "Hermetic writings" were partly composed in the 1st century A.D. But in their present form they date from around 300 A.D. and they were later multiplied by Christian writers who imitated the Hermetic manner. Though their number grew in the course of time to 20,000—one authority gives the exact figure of 36,525—they were long considered genuine.

A mere extract from this endless mess occupied 42 volumes. Only in the 17th century was it realized that the writings were forgeries and imitations. Hermetic art and philosophy remained influential for a very long time. Even today we use the phrase "hermetically closed," derived from the belief that Hermes could lock up treasures and secrets by means of magic seals and keep them out of the reach of thieves.

Hermes was also supposed to have composed two tables that became famous—the "Memphis table" and the "Emerald table." Especially the latter, which legend made Alexander the Great discover in Hermes' grave, was worshiped in the later middle ages as "Canon and true touchstone of the divine art," as a symbol and as an apocalypse. The Latin text appeared in the 13th century. Only quite recently, E. J. Holmyard discovered the original Arabic text in a genuine treatise of Jabir (8th century), while Julius Ruska found its original location in a book that was ascribed to Hermes Trismegistus and was supposed to have been discovered in his grave by Appolonius of Thyana (9th century). The actual writer seems to have been a poet and philosopher who knew the purpose of alchemy—to obtain gold through the philosophers' stone—and put it down in the mysterious language of Hermes. The Emerald table (*tabula smaragdina*) was viewed and worshiped by the alchemists as the fundamental law of their belief in the possibility of transforming metals and of obtaining gold artificially, as the revelation of the highest divine wisdom and as a key to the last mysteries of nature.

Alexandria reached its zenith as world center of Hellenistic culture and science about 500 A.D. Then the leadership gradually passed into the hands of Constantinople, proclaimed capital by Constantine the Great in 330 A.D. The Arab invasion and the conquest of Alexandria after a 14 months' siege sealed the city's fate after a history of 1000 years. Its great and famous library had, indeed, suffered previous dam-

age, e.g. in Caesar's siege of 48 B.C. and in the Christian riots of 381 A.D. when the Serapeion, the temple of the Egyptian god of the underworld Serapis, was destroyed. The Arabs, a people of horsemen and merchants, not only conquered the great metropolis but also managed to spare and assimilate its culture. They became the heirs of alchemy and its leaders in the following centuries.

### 3. *Alchemy under the Arabs* (middle of 7th to beginning of 13th century)

After the Arabs conquered other countries and settled in Spain, they devoted themselves to the cultivation of arts and sciences. In addition to mathematics and astronomy, they paid special attention to medical and alchemistic studies. The world's first public pharmacy was opened in Baghdad towards the end of the 8th century. In 755 an independent Caliphate was set up in Cordoba in conquered Spain. It became a center of Islamic civilization, from which the sciences spread to the rest of Europe. New cultural and scientific centers also arose in Italy. In the 10th century, medical schools were started in Salerno, on Monte Cassino and in Naples. "Alexandrians" taught in them, and they were specially important for the growth of pharmaceuticals. The first public pharmacy of the Christian West was opened in Salerno in the 11th century. The first European pharmacopeia was written in that city in the next century. It was the "Antidotarium" of Nicholas of Alexandria, called "Myrepsos," the head of the School of Salerno. In Germany, public pharmacies were opened in the 13th century.

J. Ruska's investigations proved that astrology and alchemy flourished in North and East Persia in the dark ages, from the 5th to the 8th century. From the cities located on the great Central Asian routes some scientists went



southwestward to the new cultural centers of Islam. Jabir ibn Hayyan, regarded by the Arabs as the highest authority, moved in the 8th century from Tus, the old capital of Khorasan, to Baghdad. He was probably the son of an Arab and a Persian woman. He was known as the founder of Arabic alchemy. The writings attributed to him were recorded towards the end of the 10th century (987) by Ibn an-Nadim in his great bibliographical collection, the "Fihrist." They were so many—several hundreds—that there were already some doubts as to the possibility of their having been written by one man. There were even doubts as to the very existence of their author. But for all that, works attributed to Jabir even increased in number over the centuries.

Towards the end of the 13th century there appeared in the West several Latin treatises ascribed to the Arabic author, whose name was Latinized into Giaber and Geber, as well as Latin translations of some Arabic writings. Only in the last quarter of the 19th century was it finally established that the Latin writings attributed to Geber did not originate in the 8th century but rather reflected the state of knowledge of the 13th century. They were henceforth known as pseudo-Geberian writings.

The French chemist Marcellin Berthelot (1826-1907) contributed to the solution of the Jabir-Geber question by publishing several Arabic writings with French translations. More recently E. J. Holmyard made his contribution. Many years of laborious work by Ruska and his collaborator Paul Kraus finally threw considerable light on this long, complex and much disputed issue. They proved that not only were Latin Geberian writings forgeries but that the Arabic writings, hitherto held to be genuine, could not possibly have been written by the historic Jabir. They were composed sometime after 900 A.D. by the adherents of the Arab religious sect called Ismailia who, in approved fashion, took Jabir's

name as author. The entire Jabir legend has thus broken down. But the content of the writings still remains important inasmuch as it offers correct information about the intellectual and working methods of the Arabic alchemists.

The most important of the Jabir writings are: "The Book of the King," "The Book of Mildness," "The Book of Weight," "The Book of Mercury," "The Book of the 70" and the "Book of the 1200." All of them contain instructions about the artificial production of gold with the aid of the "ferment of ferments," also called "elixir of elixir" (the Arabic "al iksir" comes from the Greek "xerion") or "imam" (leader). The right mixture of the four elements is required, and the "spirit" (the heated volatile mercury) must penetrate into the "bodies" (copper, lead, etc.), which is facilitated by adding some actual gold. The mysterious "elixir" itself is obtained only by the correct union of the four elements, the body (metals), the spirit (mercury), the male and the female. It assimilates the "bodies" and colors them (hence its name "tincture") by transforming them into silver and gold, up to a thousandfold quantity. It gives life to the "bodies" and resurrects the dead. The "bodies" mean the metals, except mercury, which always contain the four elements—two in an open state and two in a hidden one. To these "bodies" mercury must be added as "spirit."

The following salts and minerals are mentioned in the Jabir writings: alkali (al kaya); sal ammoniac; vitriol; orpiment; "tutia" (zinc oxide) and "kuhl" (gray antimony ore). The following chemical techniques are described: the production and purification of various metals; the sublimation of sal ammoniac and sublimate; the extraction of vegetable oils; the washing with soap and alkali, and the distillation of various liquids. The apparatus and ovens required for these techniques are also described.

Other Arabic writings that have been preserved are the

"Writings of the Loyal Brothers," i.e. of members of a secret association founded in Basra in the 10th century. They deal with the world soul and with primary substance, the four basic qualities (dry, wet, hot, cold), atoms, transformation of metals, etc. The theory of the mercury and sulfur elements is developed on the basis of philosophical assumptions. Together with the Jabir writings, with which they are connected, the "Writings of the Loyal Brothers" form a kind of encyclopedia, which had spread as far as Spain by the end of the 10th century and had a great intellectual influence in both East and West. Another writing, "Aristotle's Book of Stones," was passed as the Arabic translation of a Greek original but was actually written down in Arabic around 850. It mentions 70 minerals, garnished with magical notions.

In addition to the legendary Jabir there were other leaders of Arabic alchemy. The physician al-Rhazi, the Rhazes or Rases of the middle ages, lived about 900 and probably died in 923. He wrote a short textbook called "The Book of Secrets" which also reached Spain and, together with some texts originating in Egypt, provided the foundations of Western alchemy. The most famous of the Arabic physicians was Ibn Sina, latinized Avicenna, from Turkestan (980-1037). In his philosophical and medical writings he was an outspoken opponent of the alchemistic views; he explained the origin of gold and silver rather from vapors of the earth under the influence of sun and moon. His chief work is the great "Canon of medicine" which dominated the whole European medicine with a reputation of absolute authority in the middle ages and into the 17th century. It is still very highly regarded by the Arabs. The book is strictly systematic and carefully arranged. Another work attributed to him, the "Tractate of the Soul" which presents alchemistic views with endless repetitions and planless deviations, is obviously a forgery ascribed to Avicenna. Like the pseudo-Geberian writings it was

probably composed in the 13th century without any Arabic original. Another man worth mentioning is Ibn Rushd, usually called Averroes (1126-1198), from Cordoba in Spain. His "Commentary on Aristotle" was long highly regarded.

One of the few services of the alchemists to chemistry is the development of the art of distillation. All kinds of glass and pottery vessels were used. Greek and Arabic manuscripts give the forms of ovens, retorts and distillation vessels, with headpieces, draining and cooling pipes. The Arabic word "alembik" for the distilling helm is derived from the Greek "bikos" (a convex vessel). By improving the cooling arrangements it also became possible to obtain easily soluble distillates as liquids. This art was especially practiced at Salerno, where the distillation of alcohol was successfully achieved around 1150. This was first reported by the Magister Salernus, a scientist who died in 1167 and whose real name remains unknown. All data about the knowledge of alcohol in the early middle ages are based on a misunderstanding. Alcohol, the "spirit" obtained from wine was called "hot water" (aqua vitis) because it flowed out of cooling pipes that were twisted like vines: or "water of life" (aqua vitae), because it was used as medicine for dangerous diseases. It played a great part in combating the "Black Plague," a pulmonary disease that ravaged the West in mid-14th century. The name "alcohol" was first used by Paracelsus in the 16th century. It comes from the Arabic "al kuhl," meaning the finely ground antimony powder used as face cream by Arabic women.

#### 4. *Alchemy in the West in the Age of Scholasticism* (13th to beginning of 16th century)

Arabic culture in Spain and Italy gained more and more contacts with the Christian West. And so alchemy reached

France, Germany and England by the 12th century. This was the so-called Age of Scholasticism. But the heritage of antiquity in the natural sciences reached the West not only through the Arabs but also more directly through the work of the monks copying ancient manuscripts, including those of the classical writers. Two Latin writings dealing with different types of dyeing deserve mention here.

One is called "Mixtures for coloring mosaics" (*Compositiones ad tingenda mosaica*). The oldest manuscript dates from the 8th century and was discovered in the 18th century in the Lucca library. It contains a chaotic arrangement of prescriptions, partly of Byzantine origin, for the extraction of metals from ores, the coating of base metals with gold and silver and the composition of alloys. Among the alloys mentioned is the "*compositio Brundusii*" of copper, lead and tin, i.e. bronze. The other writing, called "The Key of Dyeing" (*Mappae clavicula*) exists in two forms, a shorter in Schlettstadt and a longer—the Way manuscript—in England. The prescriptions about obtaining alloys looking like gold and silver, including the "*compositio brondisina*," are of Greek-Byzantine origin. There are also prescriptions about the manufacture of fire arrows and fireworks from resins, mineral oils, etc; but saltpeter is not yet mentioned. The Way manuscript contains, in addition, a prescription for obtaining alcohol by distilling old and strong wine with one third of salt added.

The first Western writing to contain an alchemistic prescription is the "Schedule of diverse arts" composed by the priest Theophilus towards the end of the 10th century and one of the most valuable medieval works. It describes the manufacture of various metal vessels used in churches—chalices, censers, bells—as well as of stained window glass. Two prescriptions, in a mysterious language to be understood only by the devotees, are given for the manufacture of two kinds of gold, the "Arabic" and the "Spanish." Nothing more

is known about the author, Theophilus, who is presumed to have been a Greek.

The first mention of an alchemist in Germany dates from 1063, when a baptized Jew called Paulus appeared at the court of Archbishop Adalbert of Bremen and claimed to have learned in Greece how to transform copper into pure gold. He promised to manufacture gold coins but was treated as a liar. He remained an isolated figure and alchemy came to dominate the West only much later.

Alchemy was a closely guarded secret of the Arabs for many centuries. But when the Spanish rulers conquered some Arab scientific centers and laid hands on their libraries, the books became available to Christian scientists. Their first task was to translate the Arabic texts into Latin. It was through such Arabic texts that Aristotle finally reached the Christian West and became, as the "Stagirite" the final authority during the rest of the Middle Ages. One of the most famous schools of translation was founded by King Alfonso VI of Castile in the city of Toledo after its re-conquest (1085). Gerard of Cremona was its head.

Among the Latin translations from the Arabic is the "Book of Alums and Salts" dating from the end of the 11th century and falsely ascribed to al-Rhazi, because it follows his arrangement of the matter relating to minerals. It was also the theory of the Jabir writings that the metals were formed from mercury and sulfur in the interior of the earth through a thousand years of "cooking" but can be thus fashioned in a day by alchemy. The Arabic institutions of learning in Sicily and Italy also played their part in transmitting to Europe a knowledge of alchemy considered as part of the general natural science.

The most important writing of the 12th century is the "Assembly of philosophers" (*Turba philosophorum*) which is preserved in three versions. According to Ruska's thorough

researches it is the Latin translation of an Arabic original composed by an unknown scientist between 750 and 1150. It reports a fantastic gathering of Greek philosophers and famous alchemists presided over by Pythagoras. They discuss the transformation of metals in order to put an end to the confusion caused by the prevailing use of alchemist pseudonyms. The names of the various philosophers are mostly distorted in the passage from Greek to Latin via Arabic so that they can hardly be recognized. This "pythagorean synod" which was, in spite—or perhaps because—of its being difficult to understand, accepted throughout the Middle Ages (German translations still appeared in the 17th century). could be interpreted, modern style, as a world congress for chemical nomenclature.

Western alchemy flourished in the 13th and 14th centuries when various European countries produced distinguished leaders. Since the Church was then the bearer of culture and the protector of science, they were, as was only to be expected, priests. The cloisters fostered the arts of reading and writing and they educated the scientists in various fields. Among the natural sciences they promoted alchemy.

The leading alchemist of Germany in the 13th century was Albertus Magnus (1193-1280). He was the younger son of the Count of Bolstaedt from the Swabian town of Lauingen (30 miles below Ulm, on the Danube) and was a Dominican. He lived in many Dominican monasteries (Cologne, Hildesheim, Freiburg, Regensburg, Strasbourg and Paris) and stayed several times in Rome, where he was much in the company of his famous pupil, Saint Thomas Aquinas (1225-1274), who was also an active alchemist. As a Dominican provincial Albertus traversed the whole of Germany on foot, studying mineralogy, botany and zoology. From 1260 to 1262 he was bishop of Regensburg. He spent the last years of his life in a monastery near Cologne, where he performed his

famous feat of producing a flower garden in the middle of the winter for the delectation of the visiting emperor Rudolf of Hapsburg (he probably did it with heated nurseries). The "medieval Aristotle" was among the cleverest scholasticists. He grasped the whole knowledge of his time, in natural sciences as well as in humanities, and so also knew alchemy. His multifarious knowledge earned him the title "Universal doctor."

In the judgment of his contemporaries, Albertus was "great in magic, greater in philosophy and greatest in theology." Some works ascribed to him proved forgeries, e.g. "Of the wonders of the world," in which, among others, saltpeter, gunpowder and fireworks are mentioned. On the other hand, "Of minerals," containing Arabic and Aristotelian views and theories, is undoubtedly genuine. If it does not speak of his own experiments, it stresses the advantages of sublimation and distillation and describes the apparatus used in them, e.g. the water bath (*vas aquae bullientis*) and the distilling helm (*alembicus*). Albertus does, indeed, believe in the artificial production of gold but he also said that he had never met an alchemist who managed to obtain complete transformation. All the gold and silver samples that he tested could not pass the strongest fire test. He therefore proclaims that those who claim to make gold are swindlers. The true alchemist, he says, is Nature, and her work can at most be supported by "medicines."

England produced at that time the important Franciscan Roger Bacon (about 1210-1292), the "doctor mirabilis." Born in Somerset, he first studied at Oxford. From 1240 to 1250 he lived in Paris where he studied Arabic and Jewish writings, especially the commentators of Aristotle (Avicenna, Averroes, etc.) and continued his early studies of natural science. After his return to England he became a Franciscan but his fiery nature was little suited to monastic life and his



studies were hardly compatible with the rules of his order. As he used ground glass and transparent minerals (quartz, beryllium) for purposes of magnification—he forecast our spectacles—prepared automatic apparatus and was otherwise in advance of his time, he was supposed to be in league with the devil. His maxim, “Nothing can be sufficiently known without experiment” made him an outspoken representative of the inductive study of nature.

Bacon distinguished between “practical” and “speculative” alchemy. Like Albertus he probably knew, from the fire book of Marcus Graccus, “The book of fires to burn enemies” (written in the 13th century and not, as was previously thought, in the 8th or 9th), a mixture containing sulfur and saltpeter. He describes it in detail in his “opus maius” and reports about it in a letter written in 1265 to the Archbishop of Paris. But the mixture was not yet used as “gunpowder”; further discoveries were still needed. In addition to the “opus maius,” Bacon wrote the “opus minus” and the “opus tertius.” His monastic superior scolded him, he was banished to a Paris monastery where his fellow monks humiliated him, and he spent the last 15 years of his life in jail. Bacon believed in the philosopher’s stone but he wanted to wrest Nature’s last secrets through experimental investigations. He thus wanted to combine mysticism and natural science.

The greatest French alchemist was the Dominican Vincent of Beauvais (Vincentius Bellovacensis, 1190-1254). The chief work of this polygrapher, who was a confidant of Saint Louis, was the “Quadruple Mirror of Nature.”

The Spaniard Arnold of Villanova (about 1238-1311) enjoyed a great reputation in Western Europe. He first taught at Barcelona University, was expelled because of his provocative views, spent some time in Paris and various Italian cities, and then found a refuge in Sicily with the King of Aragon who governed the island. He was in close contact with Pope Boni-

face VIII, himself an adherent of alchemy, and came under the papal ban long after his death as a heretic and a wizard.

As the most respected physician of his time he treated Boniface for painful gallstones, and was called to Avignon by his successor Clement V. He died on the journey in a shipwreck within sight of the French coast. His chief work, in which he expounds his alchemistic views, is called "The Book called the Treasure of Treasures and the Rosary of Philosophers."

Arnold applied both magical and chemical preparations, e.g. mercury preparations, also the "potable gold" (aurum potable) or "gold water" (aqua auri). This medicine, which played an important part in medieval healing, actually contained no gold. It was a strongly sugared alcoholic solution of various spices, which shimmered like gold. He also busied himself with producing volatile oils by distillation and with the production of poisons (he wrote a book "On poisons"). He made the famous boast that "he could dye the sea if it is mercury;" but a similar boast is already contained in the "Assembly of philosophers."

Besides, these words were formerly attributed to another Spaniard, who was boosted by all kinds of myths and legends and who went down to history as "doctor illuminatus" or even "illuminatissimus." This was Ramon Llull (Latinized into Raimundus Lullus, 1235-1315), born of a noble family at Palma in Majorca. He first led a pretty dissolute life as officer and courtier, then devoted himself to intellectual activities in monasteries like Santiago and Montserrat and at the universities of Paris and Montpellier. After several adventurous trips to the Orient, he met a martyr's death in North Africa, whither he had gone as a Franciscan friar to preach the Gospel to the infidels. He was 80 at the time. Most of the 500 writings ascribed to him are forged, especially those on which his miraculous fame is founded. In the genuine works like the "Great Art" (ars magna), Llull shows himself an

outspoken opponent of the Islamic teachings of Averroes and of alchemy generally. He was the first to use individual letters and special signs like triangles, rectangles and circles to designate certain concepts and objects. He tried to found a science of discovery and invention based on scientific system and logical combination.

The forged writings of Llull, including the "Testament" which was long held genuine, describe, on the contrary, at length how a small quantity of "tincture" or "medicine" can transform mercury into a thousandfold quantity of a red powder, which can in turn transform a thousandfold quantity of mercury and so on, until finally pure gold is reached, of a better quality than the genuine article.

The so-called Geber writings, five Latin texts attributed to the legendary Arab Jabir ibn Hayyan, appeared in the West about 1300. They are called:

1. The sum of the perfection of the magisterium
2. On the investigation of perfection
3. On the finding of truth
4. The Book of furnaces
5. The Testament of Geber

As mentioned above, these writings do not date from the 9th century but from around 1300. In any case they were unknown to the great 13th century alchemists. Like so many alchemist treatises they were forged under a famous name, and are now called the Pseudo-Geber writings. They are important for the history of alchemy as they give information about the practical and theoretical knowledge of the time.

They give as primary substances the three "spirits," mercury, sulfur and arsenic. There is a new idea that ten "medicines" are required to ennoble metals and that a single universal medicine can be found for these ten through difficult and expensive labors. Numerous improved methods and apparati are described: better ovens and retorts, ash baths for

evaporation, devices for filtration, melting, sublimation, distillation, crystallization, etc. Also instructions on the preparation of milk of sulfur, mercury oxide, sublimate, cinnabar, silver nitrate, lead acetate and other acetic salts.

Most important of all, "On the finding of truth" contains instructions on the preparation of hitherto unknown mineral acids: sulfuric acid is obtained by strong heating of alum and nitric acid by heating a mixture of alum, copper vitriol and saltpeter. This "first water," "strong water" or "dissolving water," with which silver can be separated from gold, becomes, through the addition of sal ammoniac, "second water" or "royal water" (aqua regis) which also solves the king of metals and the otherwise insoluble sulfur. The oldest manuscript of the Pseudo-Geber writings is at Munich; another one is at the Vadian Library at Saint Gallen in Switzerland. Their contents were widely known in the 14th century: the first printed edition came out in 1481 and was followed by others.

From about the same time dates the collection "For the preservation of health" by Vitalis de Furno (about 1247-1327), from Four in Brittany, a Franciscan who became a cardinal and bishop of Albany. A manuscript found in the monastery library at Eberbach was printed at Mainz in 1531. The book gives extracts from authorities known to the ancients till about 1150. Among many other things it describes nitric acid and royal water. These acids were grouped, without any definite names, as "artificial waters", to which alcohol (aqua ardens) is added. The information about nitric acid dates, in all probability, not from the first half of the 12th century, but was interpolated later. A connection with the pseudo-Geber writings may be assumed but has not yet been proved.

The 14th century saw an invention that had an extraordinary military, political and economic effect on the West: fire-

arms. The invention of gunpowder used to be attributed to Berthold Schwarz (Bertholdus Niger), a Franciscan who lived at Freiburg about 1350. But gunpowderlike mixtures were actually known much earlier. The first forerunner of gunpowder was the so-called "Greek fire," invented by the Byzantine engineer Callinicus and first used in defending Constantinople against the Arabs in 678. It was a mixture of easily inflammable mineral oil, asphalt, resin, etc. with finely ground burned lime which set on fire by the heat developed through contact with water. The swimming firework carried the flames to enemy ships. The mixture probably did not contain saltpeter.

The first description of actual gunpowder is contained in the "Fire book" of Marcus Graecus about 1250. Such powders containing saltpeter served at first as inflammatives for fireworks and rockets and were first used in China. A Chinese report of 1255 mentions a "lance of intrepid fire," a bamboo tube filled with gunpowder. This is perhaps the first mention of a firearm.

The first documentary mention of guns in Europe dates from the 14th century. They were unknown when an (abortive) Crusade was planned in 1321. But in 1331 we are told that the city of Cividale in Northeast Italy was besieged with guns by German knights from Friuli, though in vain. The first mention of employment of firearms on German soil dates from 1365 when Duke Albert II of Grubenhagen successfully defended his fortress Heldenburg (near Salzderhelden in Hanover) with a "Blybuss" (blunderbuss). But from then onwards development was so rapid that by the end of the century the bigger towns were armed with large-caliber cannon.

## 5. *Decline of Alchemy and its Epigones*

Alchemy reached its peak in the 13th and 14th centuries, when Western Christian culture reached its zenith with the glories of Gothic architecture. After that, it sank more and more into a hopeless confusion. As the labors performed with a good deal of mystery monging in the "black kitchens" proved ever unsuccessful, the original sincere desire to find the philosopher's stone and to solve the great mystery turned to disappointment, confusion, insincerity and finally downright lying. External appearances were kept up and the impression given that colossal results were to be reached any moment. Writings were still published in the old-established unclear, mysterious and confused manner and ascribed to famous or invented authors—but they contained nothing new.

While the delusion of alchemy was generally kept up, critical voices were raised against it in the 14th century. Papal bulls forbade alchemy, and alchemists were threatened with excommunication at a Dominican general council. Some secular rulers, like Alfonso X, of Castile also forbade the practice of the black art. Dante, Petrarca and other leaders of the Renaissance were outspoken opponents of the alchemists, whom they described as criminal forgers. The German humanist Sebastian Bryant ridiculed them in his "Ship of Fools" (1491). For all that, alchemy continued to flourish: Paris and the universities of Northern Italy fostered it in the 14th century.

The knowledge of chemistry was not actually increased in the 14th and 15th centuries. We must glance in this connection at some writings attributed until very recently to the 14th century and mentioning, in addition to the usual stuff, matters that were actually unknown at the time. The first of these is "Of the great stone of the primeval ancestors" (Von dem grossen Stein der Uralten), allegedly written by the Bene-

dictine Basilius Valentinus at Saint Peter's at Erfurt. It was printed in 1599 by the Councilor Johannes Thoelde at Frankenhäusen in the Kyffhäuser area. Other writings, to a total of 20, were later printed in Basilius' name. The most interesting is the "Triumphal Chariot of the Antimony Brother Basilius Valentinus," later translated into Latin as were some of the others. Repeated reprintings were made up to the middle of the 18th century. The writings mention, in addition to various antimony compounds, the metals zinc and bismuth as well as hydrochloric acid, all of which were unknown until the 16th century. The riddle was only solved by the thorough investigations of Karl Sudhoff.

The writings are indeed of a later date: by some means or other they fell into the hands of Thoelde who perhaps published them in good faith. In only one case could the origin be placed: "The Last Testament" (not published by Thoelde), first printed in 1626 and re-published in an extended version in 1651. It is based on the "Booklet on Mining" published at Zerbst in 1601 by Nicolas Soleas. But since the Benedictine Basilius still continued in historical accounts, he was nicknamed "the Indestructible."

A similar part was played for a long time by the writings of Isaac and John Hollandus, father and son, supposed to have been written in the 14th century and published in the 16th. Some titles are: "Mineral Works," "Vegetable Works," "On the Spirit of Urine" and "Of the philosophic stone or elixir." The philosopher's stone is described with all its effects, including medical. Nothing definite has been established about the actual writer in spite of considerable research but he must have written them towards the end of the 16th century.

The "Easter Walk" in Goethe's *Faust* gives the best description of alchemist activities inasmuch as they were concerned with the production of medicines:

My father was a darkly honorable man  
Who meditated on Nature and the holy circles  
With the indefatigability of a cricket,  
Honestly but in his own fashion.  
In the company of other adepts  
He locked himself in the black kitchen  
And poured contrary substances together  
According to endless prescriptions.  
A red lion, a daring suitor  
Was wed to the lily in a tepid bath  
And both were tormented from one bridal chamber to  
another  
By a fire with an open flame.

While the age of alchemy was over about 1500 this does not mean that there were not any alchemists after that date. On the contrary, alchemist concepts and activities had an extraordinarily tough life: not so much as regards the panacea as in connection with the artificial production of gold. Alchemists and their mysterious goings on were welcome at the courts of German princes. German emperors of the 16th and 17th centuries—Rudolf II, Ferdinand III and Leopold I—had their court alchemist. (A street of goldmakers still graces Prague castle.) So had most of the other German rulers—the Dukes of Württemberg, Saxony-Weimar, Holstein, Mecklenburg, etc., also the electors of Brandenburg, including Joachim II, Johann Georg and the Great Elector. Even Frederick the Great, one of the most lively spirits of his time, was moved by shortage of funds to support the dark art for a while; though he did confess after his final disappointment: “I feel very much ashamed.” Some of these “goldmakers” managed to collect considerable wealth with their swindles; others ended on the gallows. Still others managed to avert this sad fate by restoring the faith of their princely breadgiver



through some positive achievement of their experiments: it was thus that Kunckel invented ruby glass and Boettger porcelain.

But the wish dream of artificial gold has continued into our days. Not only did swindlers like "Count Cagliostro" earn a living this way; Arnold Kortüm (1745-1824), the poet of the "Jobsiad," founded a Hermetic Society at Bochum and a Rosicrucian Society was founded at Königsberg in 1805. Many scientists continued to believe that transformation of metals was possible, among them Karl Chr. Schmieder (1778-1850) of Kassel who published a "History of Alchemy" in 1832. In the 1920's, there was the trial of Frank Tausend, a swindler who claimed to be able to make gold and who obtained for this purpose considerable sums of money not only from "men in the street" but from a number of otherwise very intelligent and highly placed people.

Nor is recent science free from epigones of alchemy. In 1780 the Copenhagen Academy of Sciences awarded a prize for a book on the decomposition of metals. And the German chemical world went into an uproar in 1923 when a Berlin University professor announced that he and an assistant had managed to turn mercury into gold by treatment with electric current. Not only did a number of people find "proofs" of this feat (as often happens with great inventions) but a number of "scientists," some of them all the way from Japan, claim to have performed the feat before the professor. After thorough investigation lasting two years it was finally established that the small traces of gold actually present in the electrically treated mercury (which was quite free from gold at the start of the experiment) came from the substances used by the professor, especially the iron electrodes. They meant that the "dream of gold" was finally dreamed out after 1000 years.

But the latest developments in physics and chemistry have

demonstrated that Aristotle's concept of the transmutation of elements which the alchemists have vainly tried for so long to realize was not as eccentric and absurd as it seemed only a few years ago. New investigations following the discovery of radium (1898) have completely changed our concept of the element, while nuclear physics has lately managed to split atoms, to transform elements and to manufacture artificially new elements both inside and outside the periodic system. And so the old alchemistic dream has been achieved and surpassed by reality, even though with very different means. But, even so, nobody has so far succeeded in making gold.

### III. *PERIOD OF IATROCHEMISTRY* (Beginning of 16th to middle of 17th century)

The middle ages gave way to the modern era about the year 1500. The history of natural science also took a new turn. The invention of printing (about 1450) accelerated the circulation of intellectual products; the discovery of America (1492) extended the external viewpoint, the Renaissance and the Reformation the internal. Man turned from the enclosed and musty chambers of scholasticism to the freshness and freedom of Nature. The ancient world was discovered afresh and man wanted to be "born again." He awoke from his mental twilight and viewed his condition with horror.

Faust, shaken from his stupor, exclaimed:

Ah, am I still confined in prison?

Oh, damned and dank hole in the wall!

The Reformation wanted to break religious chains, humanism to revive the spirit of antiquity. "It is a joy to live, the sciences are awake once more!" cried Ulrich Von Hutten. Natural science, too, felt a new spirit. Men wanted to learn about Nature not from mildewed pages of books but by experiencing it directly. The old authorities were overthrown.

Man wanted to break out of the sticky air of the study cabinet and the smoke of the kitchen:

Where can I grasp you, infinite Nature?

Where, you beasts, you sources of all life?

The new spirit was, as is usual in such cases, personified in a single man. He consciously opposed the ways of thought

and life of his contemporaries. As a fanatical revolutionary he ruthlessly pursued his aim and suffered the usual fate of a stormy renewer: his external life was a failure.

### 1. *Paracelsus and his successors*

The full name of this remarkable man was Philippus Aureolus Theophrastus Bombastus ab Hohenheim, but like so many other humanists, he chose for himself the Greco-Latin name of Paracelsus by which he is mostly known. He was born shortly after the discovery of America, in 1493 or 1494, at Einsiedeln in Switzerland, which gave him still another name—"Eremita."

His father, of the old Swabian noble family of the Bombasts of Hohenheim (near Stuttgart), settled as a physician at Einsiedeln and married the daughter of the monastic serf Ochsner. Ten years later he moved with his wife and nine year old son, the only offspring of the marriage, to Villach in Carinthia. There he entered the service of Count Fugger and, in addition to his medical practice, taught analysis at the local mining academy. The boy was taught by his father and at a neighboring monastery. He also could study mining at first hand and eagerly acquired the existing knowledge of natural sciences from books like that of the famous abbot Tritheim. Then he travelled for several years. Of his medical studies it is known only that he finally earned his doctor's degree at Ferrara.

But Paracelsus turned more and more from the study of books to the study of nature. "How can one," he asked, "get beyond the preliminaries of Nature, when one does not see her where she is?" He personally visited England, Sweden, France, Spain and Portugal, travelled to Poland and Russia, and, it is said, visited Constantinople and Rhodes. As he put it in his "Fourth Defense of my Travelling": "And so I be-

lieve that I deserve praise rather than blame for having spent my time so far in mere travel. I call upon Nature to be my witness. Who wants to know her thoroughly must stamp on her books with his feet. Writing is learned through its letters and Nature through her countries; each country is a leaf in the book of Nature and has to be turned accordingly."

He finally settled as a physician at Strasbourg: there is a document dated December 5, 1526 by which the city council grants him citizenship. But he had meanwhile moved to Basel where he was fortunate in curing a highly respected bookseller, Froben. Through Erasmus, who was Froben's house guest, he obtained the post of city physician and simultaneously taught at a medical academy which the city council seems to have founded in addition to the University. He attacked the traditional authority of Galenus and Avicenna and introduced another innovation by lecturing in German—Latin was hitherto the international language of science and of teaching. He earned the bitter enmity of the Basel physicians and university professors by his ruthless behavior and by his merciless sneers at their mannerisms and their red coats. Following Luther's example, he and his students made a bonfire of "the sum of books" on Saint John's Day of 1527. "so that all misfortunes should vanish into thin air with the smoke." We don't know whether the books he burned included Avicenna's "Canon of medicine" or any other respected work of Arab-Hellenistic science. In any case, Paracelsus got involved in violent quarrels, was slandered by some friends and pupils and finally had to flee from Basel in February 1528.

After a brief stay at Colmar in Alsace he spent some time at Nuremberg and other cities. From 1531 onwards he led a wandering life without a fixed residence. He mostly travelled on horseback, his sword at his side, spent a good deal of his time with fellow vagabonds at inns and taverns and more

often than not drank more than was good for him. But through all wanderings he never lost sight of his aims: the study of natural phenomena and the renovation of medicine. During short periods of rest he wrote some books and dictated others. From 1535 he became interested in religious questions, on which he also wrote. And he practiced medicine whenever an opportunity offered itself. In the late summer of 1541 he came to Strasbourg, prematurely aged, a decrepit old man at 47. He left his few belongings to the poor and homeless and gave up his restless soul on September 24, 1541, forever true to his motto: "Let no one be different who can be himself."

The following are the most important of Paracelsus' numerous writings: "Archidoxa," "Of the tincture of the physicians," "Paramirum," "Paragranum." "The treasure of treasures of the alchemists," "Of the diseases arising from tartar" and "Great Wound Surgery." Many writings were falsely attributed to him. Sudhoff traced no less than 376 editions of his writings. He and Mathiesen recently produced a critical edition of Paracelsus.

Paracelsus acquired a thorough chemical knowledge through his experiments. In his medical practice he started from the assumption that all the processes of life are of chemical origin and can be chemically influenced. It was he who used for the first time the German word "Chemy" instead of "Alchemy" (1528). Still, he took over the basic alchemistic elements, mercury and sulfur, to which he added salt. Mercury was for him the principle of the heavy, fluid and volatile, sulfur that of the inflammability and of heat and salt that of the ability to withstand fire and to dissolve in water. These three principles or "tria prima" compose, in varying mixtures, all mineral substances, plants and living creatures. Diseases appear when the right proportion of the mixture is upset. Too much mercury causes paralysis and melan-

cholera; too much sulfur—hotness and fever; too much salt—dropsy and diarrhea. The upset balance can be restored by the introduction of suitable chemicals and the disease thus cured. He says in his "Paragranum": "It is not as alchemists say: make gold and silver; but rather: make medicines and cure diseases." Instead of the Galenian concoctions, decoctions and mixtures he introduced chemicals as medicines, including especially some heavy metal salts that were hitherto only known as poisons.

He also demonstrated how dosification influences the effects of the substances applied. He introduced arsenic compounds and various salts of copper, lead, mercury and antimony into the pharmacopeia. Mercury salts proved specially effective in combatting syphilis, a venereal disease that then devastated humanity. It was probably brought back by Columbus' crew as the New World's first gift to the Old and then spread by the French troops fighting in Northern Italy, so that it was called "the French disease."

Paracelsus also used other chemicals as medicines, e.g., milk of sulfur and the spirit of wine, on which he bestowed the name of "alcohol," from the Arabic word meaning a finely ground powder. He also applied a mixture of alcohol and sulfuric acid, which was much used in later years under the name of "Haller's acid" (*Elixir acidum Halleri*). He also stressed the need to purify the various substances used and to complete by suitable treatment the effect of Nature's medicines. He already experimented with extracting the active part of various drugs and medicinal plants as their "fifth essence." By placing chemistry in the service of medicine he founded iatrochemistry and the pharmaceutical chemistry that later developed from it. He also recognized poisonings by lead and other noxious substances and thus founded scientific toxicology.

But for all these basic innovations Paracelsus remained in

many ways a man of the middle ages. The four elements of Empedocles still play a part in his work side by side with the "tria prima"; the "three principles" are composed of them. A special spirit, "Archeus" is said to regulate digestion. Another, called Tartarus (the name of potassium acid tartrate and also of the Greek god of the underworld with its torments), is supposed to cause gout and similar ailments. Paracelsus proclaimed chemistry, philosophy, astrology and virtue to be "the four columns of medicine." He always stressed the great importance of chemistry: "No physician should be without this art." But it was a long time before his views prevailed over the resistance of academic medicine and of the medical profession. The first official German pharmacopoeia, the "Dispensatorium pharmacorum omnium." by Valerius Cordus (1515-1544) who also first produced sulfuric (ethyl) ether in 1540, is still written in the spirit of Arab-Galenian medicine. The new medicinal plants and woods from America found a readier welcome in Germany. Chemical medicines were to be found in pharmacies only around the end of the 16th century.

The adherents and successors of Paracelsus were men of varied character. Some were boasting charlatans who imitated the master's rough manner and unconventional mode of living but did more harm than good by their clumsy application of his new chemical medicines. Their effect was that of a pestilence. But there were also among them men who practiced their profession with a sense of duty and scientific understanding. Their work was indeed a blessing.

Much mischief was done particularly with antimony preperates. Already in 1566 their use was banned by the French Parliament, a decision confirmed by the Paris medical faculty in 1603. Some leading iatrochemists will be treated below; but it must be borne in mind that they were still agitated by the old alchemists' dreams. Some of them still acted as "gold



makers."

Among the most important was Leonhard Thurneyssen zum Thurn (1530-1596), son of a Basel goldsmith.

At first he practiced his father's trade but soon, he, too, embarked upon a vagrant life. He practiced alchemy and also medicine, without studying the latter; he was a soldier and then worked in various mines in the Tyrol. He travelled in Scotland, Spain, Portugal and other countries for the Archduke Ferdinand. In 1570 he found a permanent shelter in the Grey Monastery in Berlin, having cured the wife of Johann Georg, the Elector of Brandenburg. He spent 15 years there living like a prince. He even had his own printshop and, in addition to engaging in all kinds of trickery, did some serious research. He was the first to attempt to analyze the content of mineral waters by examining their residue after evaporation. But his alchemistic activities made a further stay in Berlin too dangerous for him and so he secretly fled to Switzerland in 1584. He died at Cologne after leading the life of a vagabond in Northern Italy and elsewhere. He was but one of the many "darkly honorable men" of that age.

A more serious scientist was Andreas Libau (about 1550-1616), known humanist fashion as Libavius.

Born at Halle, he studied at Jena where he became a doctor of medicine and a poet laureate; the time offered opportunities to men of many talents. He taught school at Ilmenau and Coburg and was professor of history and poetry at Jena until 1591, when he became city physician at Rothenburg. He was also inspector of schools there and taught at the local Gymnasium. From 1607 to his death he was director of the "Gymnasium Casimiranum" at Coburg. The following of his writings are important to us, in addition to "Logical exercises," theological treatises and Latin poetry: the "Alchemyia collecta," first printed in 1595 and repeatedly re-printed as an excellent textbook of chemistry; the analytical studies

"The Art of testing minerals" and "On analyzing mineral waters" (1579); the "Alchemistic Practice" of 1603. The word "alchemy" is used by Libavius in the sense of chemistry. His collected works on medicine and chemistry were published in three volumes in 1616.

Libavius was an adherent and admirer of Paracelsus; but a critical one. In his medical practice he avoided the abuse and misuse of chemical medicines, especially of the antimony preparates. He was a good analyst and established the silver content of lead ores; on the other hand he defended in a treatise against the University of Paris the theoretical possibility of the transmutation of metals. He analyzed mineral waters and proved that the sparkling mineral waters contained carbon dioxide. He also busied himself with chemical techniques. He obtained the "spirit of salt" by heating a mixture of salt and clay and sulfuric acid by burning sulfur and oxidizing the vapors in the air or by adding saltpeter. He proved the presence of sulfuric acid in vitriols and alums. By heating a mixture of amalgamated tin and mercury sublimate he obtained tin tetrachloride, which is still known to chemistry as the "spiritus fumans Libavii." He was also busy with other technical matters, like the manufacture of colored glass. He worked out a remarkable plan for a laboratory building with all kinds of necessary arrangements, including hygienic; but it was never carried out.

One iatrochemist occupied an official post at a German university. Landgraf Maurice of Hesse, a patron of the sciences, appointed in 1609 his former court mathematician Johannes Hartmann (1563-1631) professor of "Chymiatry" at Marburg University. Hartmann had studied medicine while professor of mathematics.

He founded the first university chemical laboratory, at which his students worked. His instructions on the making of medical preparates for laboratory teaching were published

after his death in 1633 as "*Praxis chymiatrica*." The first university laboratory was thus used in the service of iatrochemistry. Another excellent university laboratory is reported at Altorf in 1683. Altorf University was founded in 1623 by the imperial free city of Nuremberg and existed till 1809.

Iatrochemistry also flourished outside Germany. Theodore Turquet de Mayerne (1573-1655) of Geneva made his reputation as physician in Paris and became personal physician to the king of France.

It was his excessive use of antimony preparates that prompted their banning by the Paris medical faculty in 1603. To avoid the ensuing trouble he moved to London in 1611, where he became personal physician to kings James I and II and died at 82. He acquired useful chemical knowledge by experimentation. He established the inflammability of the gas produced by the application of acids to iron, without, however, characterizing hydrogen as such.

The Italian Angelus Sala (1576?-1637) from Vicenza near Venice also worked as a reputable physician and chemist outside his country, e.g., at Zurich, the Hague and Hamburg. In 1625 he became personal physician to the Duke of Mecklenburg.

He introduced silver nitrate as "*lapis infernalis*" (hell stone) into the pharmacopeia and fought against mystery-monging by publishing valuable instructions for the making of various medicines. He recognized that sal ammoniac was composed of hydrochloric acid and ammonium carbonate, also the precipitation of copper by iron and the development of nitric acid from saltpeter by sulfuric acid, etc.

The most important follower of Paracelsus was Johann Baptist Van Helmont (1577-1644), born at Brussels of a noble Brabant family. He studied at the Jesuit University at Louvain, at first philosophy and theology and later, with great eagerness, the natural sciences (mathematics, astronomy,

physics and chemistry) as well as medicine, of which he became a doctor in 1599. After travelling in France, Italy and England he returned home in 1605. He married and lived as a rich man (he was also Count of Merode) in retirement as physician and natural scientist in the Brussels suburb of Vilvorde—a complete contrast to Paracelsus. He refused the outer trappings of fame, including a call to Vienna, but had a great influence on his contemporaries. He published very little but became a European celebrity. His collected works were published only after his death by his son in 1648 under the title of “Garden of Medicine.” French, German and English translations appeared from the original Latin. A medical textbook of his, “Modern pharmacopeia and dispensary” was also published in 1648.

For all his sober observation of nature Van Helmont could not entirely free himself from obsolete notions. He believed in the transformation of metals and in the “philosopher’s stone.” He also accepted the “alkahest,” the universal solvent of the middle ages and of Paracelsus. He believed in Paracelsus’ “Archeus,” the vital spirit dominating all the processes of life. Nor was he free from all kinds of mystical notions. Thus he once said that mice could be created in a container filled with flour and dirty laundry. But for all his concession to the “spirit of the times” he was a sober and responsible natural scientist who tried to find the truth by experiment and achieved much for the development of chemistry. He might be called the founder of physiological chemistry. He also made numerous experiments to prove the law of the preservation of matter experimentally.

Van Helmont’s basic views were as follows:

Everything material has two causes:

1. The “materia,” the substratum of things, the “beginning from which”;
2. The “causa efficiens,” the “seminal beginning through

which," the true primary ferment, the inner "agens."

Matter in turn consists of two original primary substances, the "elementa primigenia," water and air, which cannot be transformed into each other. Earth is not an element and was created from water. The "three principles" of Paracelsus, mercury, sulfur and salt, are not real elements and play a secondary part. The various qualities of the different substances are based on different arrangements in space of the three "principles." This is a view that was perfected two and a quarter centuries later (1874) by another great Netherlander, Jacobus Henricus van't Hoff, by establishing the stereochemistry of carbon.

Particularly important are Van Helmont's investigations of the gases, which he was the first to distinguish strictly from vapors. Both are spirits (*halitus*) but vapors liquefy again by cold. Paracelsus had already used the word "gas," derived from the Greek "chaos"; but Van Helmont introduced it into the language of chemistry: "I call by the new name 'gas' the hitherto unknown spirit that cannot be caught in a vessel or reduced to a visible body unless its 'seed' is previously extinguished." He especially dealt with carbonic acid, which he called "gas sylvester" and sometimes "gas carboneum." He recognized that it was the same kind of gas as was developed in the action of acids on marble or potash, in the burning of coal and in alcoholic fermentation; also that it is contained in the natural sparkling mineral waters and emanates from the earth in the Dog's Cave near Naples. Its fire extinguishing effect is common to other gases like sulfur dioxide and nitric oxide. He also studied inflammable gases: marsh gas and the "kinds of air" developed in the dissolution of iron or zinc in acids or the dry distillation of organic substances—the "gas flammeum," "pingue" or "ventosum." He investigated the burning process and noted that a part of the air is consumed in it. He also made other

useful observations, e.g., that strongly heated saltpeter turns into ordinary alkaline salt and that silica heated with alkali can be converted into a water soluble smelt, from whose solution it can be again separated by addition of acid.

Two other iatrochemists should be mentioned, a Dutchman and a German. They led iatrochemistry to its ultimate height that it reached before it fell before the progress of science.

François de la Boë Sylvius (du Bois, 1614-1672), born at Hanau of a Dutch family, studied medicine and was a practicing physician at Hanau and Amsterdam, until he became professor of Leyden University in 1658. He stayed at Leyden as a highly respected teacher and physician until his death.

Influenced as he was by Van Helmont, he freed himself from the latter's partly still mystical notions (Archeus, etc.). He tried to explain all normal and pathological processes of pathophysiology without any assumption of spiritual powers but purely chemically. He explained the difference between arterial and venous blood by the action of the breathed air. He regarded the acid and alkaline content primarily responsible for the normal course of the biological processes. The predominance of the one or the other causes diseases, which are therefore to be cured chemically. The whole of medicine would thus become a kind of applied chemistry. In addition to acids (nitric, acetic) and lyes (volatile spirit of hartshorn) he used the salts of heavy metals (silver, mercury, zinc, antimony) as internal medicines. He shared with his contemporaries the belief in the philosopher's stone and the transformation of metals. In his view that sulfur was composed of sulfuric acid and an inflammable oil, he approached the later phlogiston chemistry.

Otto Tacke or Tachenius from Westphalia, whose years of birth and death are unknown, came from Herford. He first studied pharmacy then turned to medicine in Italy, whither

he went in 1644. He practiced medicine in Padua and later in Venice. He had a good chemical sense and was in this respect in advance of his time, even if he stuck to some old-established notions like that of the universal solvent alkahest.

While all water-solvent substances were hitherto regarded as salts, Tachenius limited these words to compounds of acids and alkalis. He recognized glass as a salt of silicic acid and supposed the existence of a "hidden acid" in fats and oils, almost 200 years before Chevreul cleared up the constitution of fats. We find in him the beginnings of chemical analysis by the wet process, e.g., proving various heavy metals salts in aqueous solutions by gallnut tincture, the precipitation reaction of chlorides with silver solutions and of mercury solutions with sal ammoniac or with alkali. He even carried out quantitative experiments, and established that lead lost about a tenth of its weight in transition to minium. •

Tachenius was the last important iatrochemist. Iatrochemistry increased our chemical knowledge considerably: nonetheless it was doomed to failure because it could not solve its self-imposed task of explaining all biological processes chemically. It shared the fate of its predecessor, alchemy, which had also pursued an unattainable aim.

## *2. Applied and technical chemistry in the age of iatrochemistry*

The middle ages saw, in addition to the growth of alchemy, a gradual growth of mining and smelting activities to obtain metals and other raw materials. After the invention of cannon, the gunsmiths composed the so-called firework books (*Feuerwerk-buecher*). They were often men of good family and standing and wrote not only about their special knowledge of guns and the manufacture of powders and explosives

but also on all kinds of technical matters, engineering, metallurgy, coins, etc.

Of such is the so-called "Medieval Housebook" of the last quarter of the 15th century, beautifully illustrated and of a varied content, including medical. Other kinds of books were printed as "Booklets on Distillation," "Booklets on Art and Alchemy," "Booklets on Mining," etc. They contain all kinds of prescriptions for the production of chemical products, the working of metals, pearls and jewels and all kinds of alchemistic traditions.

The author of the first textbook of chemical technology came from Italy, a land of old culture, wide trading connections and some industry (metal and glass at Murano near Venice; brass foundries in Milan; alum in the papal Tolfa near Rome). It was Vanoccio Biringuccio (1480-1538).

Born in Siena, he worked as architect, gunsmith, metallurgist and chemical technician for the city's ruler, Pandolfo Petrucci. He was an outspoken opponent of alchemy, and had a very changeable life in an area of wars and disturbances. The masterpiece of his casting was a bronze tube 6.7 meters (20 feet) long, the longest gun barrel ever cast. Biringuccio made a number of study trips, including one to Southern Germany where he visited mines and foundries. He was banished from Siena for a time, returned there to become chief architect of the cathedral, finally entered the papal service in 1538 and died shortly afterwards.

He put his wide knowledge and experience into his great work, the "10 Books of Pyrotechnics," published only after his death in 1540. It was re-published many times: up to 1678 there were four Italian editions and three French translations.

The chief representative of this tendency in Germany was Georg Agricola (real name Bauer, 1493-1555), Agricola was born at Glauchau in Saxony, studied theology, philosophy and philology at Leipzig University and then taught for



two years as "master of arts" at the city school of Zwickau. Here he wrote a Latin grammar which was published in Leipzig in 1520. His thirst for knowledge made him return to college. He studied medicine in Italy (Bologna, Padua, Venice) and after thorough medical and other training returned home, becoming in 1527 city physician to the newly founded mining settlement of St. Joachimsthal. He became particularly interested in mines and foundries. His great interest in finding out more about individual metals made him engage in an intensive study of chemistry. In 1533 he moved to Chemnitz where he became city physician and was several times elected mayor. He added so much to our knowledge of metals that he deserves to be called the founder of scientific mineralogy.

It was during the six years at Joachimsthal, which were of decisive importance for the rest of his life, that he wrote or prepared the books of which Goethe wrote in his "Theory of Colors": "they embrace all of the old and new mining, old and new metallurgy and mineralogy and seem like a precious gift to us." In 1530 he published his "Bermannus sive de re metallica dialogue" (Bermannus or dialogue on metallurgy). It is written in the form of a scientific dialogue between Lorenz Bermann, a Joachimsthal physician and a good friend of his, and two learned doctors about various ores and minerals. They discussed the question of what minerals actually represented the names transmitted from Greeks and Romans. They concluded that the actual situation must have been more complex than ancient writers like Dioscorides and Pliny made it out to be. And so one should not acquire one's knowledge from ancient writings but from one's own experience and experiments. A good deal of new information is incidentally imparted about the sources of silver, lead and other ores and especially, for the first time, about the new metal bismuth.

Several of his works on geology and mineralogy were published only 16 years later at Basel: "On the origin and causes of subterranean substances," "On the nature of fossiles," "On old and new metals," etc. "Fossiles" mean minerals to Agricola. While Agricola, as is only to be expected, generally accepts alchemistic views, he is definitely opposed to gold making. He does not yet know true chemical analysis. He describes and estimates the various ores and minerals according to their external qualities, in which taste and smell play a part. He also deals with such geological questions as the formation of mountains, their transformation by the action of water, etc. His historical and philological training make their influence felt throughout.

His chief work, which he did not live to see printed, is the "De re metallica libri XII" (Twelve books on metals), a thorough account of the mining and foundry industry of his time. It was published in Basel in 1556, illustrated with over 300 woodcuts. A German translation by professor Bechius of Basel appeared a year later. Agricola's sources are the old German "firework books," other works like Biringuccio's "Pyrotechnics" (from which he lifts entire chapters) and his own very careful observations. He thus created a textbook of mining, foundry work and chemical engineering that was in use until the end of the 18th century. The Association of German Engineers recently published an excellent German edition with faithful reproductions of the original woodcuts. An English edition was published earlier in America.

Individual chapters of Agricola's mining handbook deal in detail with assaying; the treatment of ores; roasting, production and purification of sulfur; production of heavy metals; liquation of silver with lead, separation of gold and silver, etc. There are also descriptions of the production of various chemical preparates like saltpeter, alum, green vitriol,

etc. Besides bismuth, zinc is mentioned as a new metal. It was probably first won as a by-product of the Rammelsberg mines in the smelting ovens of Goslar, and it was Agricola's textbook that first made it widely known. It was at first called by names like "Kobelt," "Conterfey" or "Cadmia metallica," while the actual word "zinc" referred mostly to the zinc ore (calamine). Like bismuth, zinc was not at first considered to be a genuine metal, especially since the holy number of seven metals could not very well be augmented by two. It was only in 1617 that Loehneyss' "Book of Mining" uses the word "zinc" unambiguously to describe the metal; but even so it still confuses zinc with bismuth.

Among the leaders of chemical technology outside Germany one should mention the Frenchman Bernard Palissy (1499?-1589) who from a simple potter became a respected scientist. He fought against reliance on authority and wanted to rely only on the results of experiments. His great services were especially to ceramics: the coating of clay with enamel; glazes with lead and tin smelts and, generally, the making of fayence (named after the Italian town of Faenza). His books "L'art de terre" (Art of clay) and "Des terres d'argile" (Of clays) were reprinted as late as 1777 and 1844. Palissy was in some respects the forerunner of Leibig. He recognized the necessity of compensating the minerals drawn by growing plants from the soil by the addition of suitable chemicals. He recommended to the farmers the use of marl as artificial manure.

The Italian Giovanni Battista della Porta (1537-1615) was a man of a very different type. A polygrapher, he gathered his knowledge from books and from extensive travels in various parts of Europe.

His chief work, the "Four books of natural magic," is a kind of encyclopedia of the natural sciences of his day. It was published in 1567. It was translated into five languages

and was published at Nuremberg in 1617 under the title of "Natural magic." Another book of great reputation was the "Subterranean Hall or description of the chief kinds of ores and mines" published in Prague in 1574 by the Bohemian mining expert Lazarus Ercker. It was used as a textbook of metallurgy for a century and a half and was reprinted as late as 1736 at Frankfurt.

The most important figure of applied and technical chemistry of the 17th century was Johann Rudolf Glauber (1604-1670). His life partly coincided with the great war that devastated Germany for 30 years and abruptly broke up all economic and cultural development.

Glauber was born at Karlstadt in Franconia. The son of a barber, he was early orphaned and led such a restless and agitated life that he was nicknamed "the 17th century Paracelsus." As with the founder of iatrochemistry, it took some time before he received a just appreciation. They were both described as typical charlatans in the "History of Human Folly" published in 1787 by the Leipzig professor Johann Christoph Adelung (1732-1806). Glauber learned to know "a considerable part of Europe," as he puts it, on his restless travels. There are few reliable data about his colorful career. He occupied various posts, including that of apothecary, at Giessen, Frankfurt and other towns. He finally reappeared in Amsterdam in 1648. There he stayed two years, married a second wife (his first marriage was a failure) and was busy in a laboratory. After peace was concluded (October 1648), he returned to his "beloved fatherland," established a laboratory first at Wertheim and then at Kitzingen and traded in wine. The elector of Mayence granted him a privilege to manufacture wine vinegar. He "freely distributed to rich and poor" antimony pantasulfide, which he called the "antimony panacea." He also published a "Pharmacopoea spagyrica" (Nuremberg and Amsterdam, 1654). He got involved in un-

pleasant quarrels and moved from Kitzingen to Amsterdam in 1654. With great enthusiasm for active investigation he set up a new large laboratory in which he employed for a time six assistants. He also used an experimental cornfield to test artificial manures. But after some years he was paralyzed and was bedridden from 1666 onwards. But he still remained active for four years until he died at 66.

Like Paracelsus, Glauber was for all his restlessness and agitations a very busy writer: he composed some 40 works. In the first years of his second stay at Amsterdam he wrote a six-volume work "Germany's welfare," published in that city from 1656 to 1661. His collected works, published 1661, included "On minerals"; "Marvel of the world" and the "Nature of salts." The 7 volumes were often republished and translated into English and French. A brief summary of his teachings was published in 1668 as "Concentrated Glauber" or "Glauber's Laboratory." Some of his later writings, as "On the three principles of metals" (1666), "Of the artist Eliah" (1668) and "Of the secret fire of the philosophers" (1669) are totally alchemistic in their contents. We meet in them the universal solvent alkahest that heals all diseases, the "potable gold" and such like concessions to the spirit of the times.

Glauber's chief importance lies in his achievement in practical chemistry. And this achievement was very great indeed. One might call him the founder of the chemical industry, not only with regard to inorganic chemistry but also the beginnings of organic chemistry. His practical activities produced so many scientific observations and concepts that this self-taught man has left his mark also on the science of chemistry.

In inorganic chemistry, Glauber's chief sphere of interest was the production of mineral acids. He published the relevant prescriptions—as far as he wished to make them public—in the five volumes of his "New philosophical furnaces"

(Amsterdam, 1648-1650). Some processes developed by laborious experiments he kept secret and, one might say, "patented," revealing them to others for a fee. He produced sulfuric acid both by the dry distillation of alum and vitriols and the burning of sulfur, in which he subjected the "oleum acidi vitrioli" to fractional distillation. He produced nitric acid as "aqua-fort," "strong water" and "spiritus fumans Glauberi." By the action of arsenious acid on saltpeter he even obtained the then quite unknown blue nitrogen trioxide, which decomposes again even under ordinary temperatures. In producing hydrosulfuric acid he obtained the "spirit of salt" in different ways (e.g., by burning salt-drenched charcoal or placing a mixture of salt and vitriol or alum on glowing charcoal); but, most efficiently, according to his secret procedure of action of fuming sulfuric acid on salt. In addition to the ordinary concentrated sulfuric acid he obtained the fuming sulfuric acid, known for two centuries afterwards as "spiritus" or "Acidum salis fumans Glauberi." The sodium sulfate, produced in the process in beautiful crystals, was particularly dear to him and he never tired of describing its wonderful qualities. It still keeps his name alive in chemical nomenclature as "Sal mirabile Glauberi" or "Glauber salt." From purified acids and bases he obtained hitherto unknown salts like ammonium sulfate, the "sal ammoniacum secretum Glauberi" and produced them by fractional crystallization in unusually pure state. Like Tachenius, he confined the concept "salt" to binary compounds of acids and bases. He also investigated the mutual conversions of various salts and, like Tachenius, attempted chemical analysis by the wet process. In neutralizing of potash and soda solutions by the addition of hydrochloric acid he used the ending of the development of carbon dioxide as "indicator."

Glauber also manufactured several compounds of organic chemistry in his laboratory which grew into a small chemi-

cal factory. He dehydrated alcohol with heated potash and subjected it, as well as vinegar and the pyroligneous acid he obtained by dry distillation, to a fractional distillation. He produced many different salts of the acetic acid including hitherto unknown products like acetone and acrolein. He also worked on coal, and close examination of his writings revealed that he managed to isolate benzol and phenol from the distillation products. He described the latter as a "hot and bloodred oil which violently dries and heals all wet ulcers." Thus Glauber appears to have discovered the antiseptic effect of carbolic acid two centuries before Lister's epochal achievement.

Glauber tried to isolate the active element of medicinal plants by treating their cut-up parts with warm nitric acid and sulfuric acid. By adding a potash solution he actually obtained the vegetable bases or alkaloids, whose discovery immortalized the name of Sertuerner a century and a half later. His reports make it quite clear that he handled morphine, brucine and strychnine. He also improved the production of aromatic oils and of tartar emetic. He also observed the presence of dextrose in honey and other natural products and proposed improved dyeing techniques. This self-taught man, relying entirely on his enthusiastically performed experiments, must be credited with extraordinary chemical achievements and was in many ways in advance of his time.

Glauber also improved the laboratory arrangements and apparatus. He not only proposed new forms of "philosophic ovens" and of apparatus for condensation and distillation but also had many implements made of clay and glass instead of metal, introducing in the process such improvements as glass plugs, mercury sealing, stirring arrangements, etc. He produced ruby glass before Boyle and Kunckel. He used for this purpose the "purple of Cassius," obtained by the pre-

cipitation of a diluted gold solution with tin dichloride and tetrachloride. It was invented by Andreas Cassius, personal physician to the Duke of Holstein (died 1673) and described in 1685 by his son who bore the same name. Of his other multifarious activities we will mention only his manufacture of artificial jewels of all kinds and his activities in the chemistry of explosives, prompted by the many wars of his time. He even manufactured fillings for a kind of glass grenade.

Glauber's interests were by no means confined to chemistry, in the laboratory or in the factory. He was very much interested in economic questions. Although his chief creative work was done abroad, in Holland, he remained faithful to Germany in spirit. The six volumes of his "Germany's Welfare" published in Amsterdam in 1656-1661 prove this conclusively and brilliantly. After the devastations of the 30 Years' War he offered good advice for the restoration and further development of German agriculture and industry. He strongly counselled that German ores, minerals and other raw materials should not be exported and then expensively re-imported in a manufactured state but should be industrially treated in Germany itself:

"Germany is well endowed by God with all kinds of mines . . . but she needs experienced men with expert knowledge. . . . Why are we so stupid that we send our copper to France or Spain and our lead to Holland and Venice to make white lead and Spanish green which we have afterwards to buy so dearly? Is not our German wood, sand and ash as good for the making of crystalline glass as those of Venice and France?"

Glauber was not only a wide-awake industrial chemist but a German patriot concerned about his fatherland.



### 3. *Transition to Independent Chemistry*

The more the iatrochemists insisted that all biological and organic processes are to be interpreted as chemical phenomena, the more they revealed the inadequacy of this viewpoint through the lack of relevant chemical knowledge and thus hastened the decline of iatrochemistry. The scientific spirit of the modern age stressed instead inductive reasoning and experimental empiricism. Among them was Leonardo da Vinci (1452-1519), the universal genius, and Luis Vives (1492-1540), the Spanish philosopher. Paracelsus, too, belonged to this tendency, even if his mental outlook remained medieval. But the most representative leader of the new tendency was the English philosopher and statesman Francis Bacon of Verulam (1561-1626) who asked that "spirit and senses be cleaned of abstract prejudices and all investigation reduced to experience."

Opinions are divided about Bacon's real importance for the development of natural science. Justus Liebig strongly argued against him in his Munich Academy speech of 1863. But for all such reservations, Bacon plays a leading part in the history of natural science as the reviver of the atomic theory. He expounds his views on the material composition of things in his "*Novum Organum*" (1620). The smallest parts of which bodies are composed are for him not, as they were for Democritus, atoms equal in quality and moving in empty space, but the ultimate and contiguous particles of the visible and tangible body. They differ from that body only in size. Bacon calls them "*corpuscula*," corpuscles. He founded the corpuscular theory.

The first adherent of this theory in Germany was Daniel Sennert (1572-1637) of Breslau, professor of medicine at Wittenberg at the beginning of the 30 Years' War. An eager adherent of Paracelsus and of the experimental method, he

stressed the importance of chemistry in medicine and rejected the mystical speculations and partly absurd views of his master. In his "Agreement and disagreement of the chemists with Galenus and the Peripatetics" (1619), Sennert develops an atomic theory based on that of Democritus. His "atoma corpuscula" or "corpora individua" are not mathematical points in an empty space but have three dimensions: they represent both the last degree of division and the first degree of composition of physical bodies. He sees experimental proofs of his view in the formation of smoke and the processes of sublimation and dissolution. He stresses for the first time the concept of a chemical substance as something stable under all compositions and transformations. This theory of the immutability of elementary parts became, together with Galileo's mechanics and its concept of force, the foundation of theoretical physics and chemistry.

And yet Sennert pays his tribute to the Empedoclean theory of the four basic elements: fire, water, air and earth. The various chemical elements are composed of them as "prima mixta." The concepts of atom and elements could be clarified from the ancient conceptions only gradually. Sennert was attacked for his "heretical" views: he openly proclaimed that he did not recognize Aristotle as absolute authority because truth consisted in the agreement of concepts with things and not with other people's concepts.

The medieval conceptions were so cleared away in the leading intellects of the 17th century that a new age could dawn for chemistry.

#### IV. INDEPENDENT CHEMISTRY TO THE DISCOVERY OF OXYGEN

(Middle of 17th to last quarter of 18th century)

Everything done in chemistry had hitherto been done on certain definite assumptions and for certain definite practical purposes. One did not ask questions of Nature to establish the qualities of different substances. The alchemists wanted, in all kinds of ways, to produce the philosopher's stone and to transmute base metals into gold; the iatrochemists engaged in chemistry only to find useful medicines and to solve problems of biology and physiology with quite inadequate means. They, too, had to fail because their aim was unattainable.

##### 1. *Foundation of Independent Chemistry by Jungius and Boyle*

Transitional periods, in which the old dies and the new comes up, generally produce individuals whose character and activities reflect the new age and who become its leaders. Of such was in Germany Joachim Jungius (real name Jung, 1587-1657), a contemporary of Sennert. Jungius' true importance, like that of Paracelsus, was only realized quite recently—in his case through Paul Walden.

Jungius was born at Lubeck and studied philosophy and mathematics at Rostock. He became professor of mathematics at Giessen at 22 but gave up his post after 5 years. After long stays at Augsburg and Lubeck he studied medicine at

Rostock and became doctor of medicine at Padua in 1619. He practiced medicine at Lubeck and Rostock, founded a learned society called "*societas ereneutica*," became in 1623 professor of ethics and mathematics at Rostock and two years later professor of medicine at Helmstedt. In 1628 he became the rector of a Hamburg Gymnasium, the Johanneum, a post at which he remained till his death. He was a man of many-sided talents in the natural sciences: he did some fundamental work in botany by developing concepts of genus and species and laying the foundations of the later Linnean terminology. He was a determined opponent of scholasticism. Leibnitz judged his importance to be comparable to that of Copernicus and Galileo.

Like Sennert, Jungius adhered to the Democritean atomic theory revived as corpuscular theory and expounded in special dissertation in 1642. In another dissertation of the same year he gives the first definition of the concept of element in the sense still valid today—a unitary substance that cannot be further decomposed. He explains the different properties of bodies of the same composition by different arrangements in space, thus forecasting the modern concept of isomerism. He explains the chemical transformation of one chemical element into another by such "*metasyncrisis*" but rejects the transmutation of metals and the "*tria prima*" of Paracelsus. He was the first to explain correctly the red coloration of a clean iron staff in a blue copper vitriol solution by stating "copper atoms replace iron atoms." He also stressed the importance of scales in determining the weight ratios in chemical processes. His chief work, the "*Doxocopia physicae minoris seu Isagoge physica doxocopiae*" appeared only after his death (1662), and so did his "*Isagoge phytoscopiae*" (1679).

The leading figure of the new age in England was Robert Boyle (1627-1691) who is generally regarded as the founder of independent chemistry. He was born as the fourteenth

child (seventh son) of a distinguished noble family at Lismore, County Waterford, in Ireland, and received a thorough education at Eton College.

At the early age of 11 he left, accompanied by his tutor, on the customary "grand tour" of English noble families. He went through France and Switzerland to Italy. During long stays at Geneva and Florence he studied law, philosophy and theology, and also mathematics and natural science. Called back home after 8 years' absence because of the Cromwellian troubles, he found his father dead and the property devastated (1646). He lived for years in his solitary rural retreat, occupied himself with problems of religion and natural science and wrote a book on ethics. He moved to Oxford in 1654 and to London in 1668. There he became a member of a society for the study of natural science founded in 1660 by the Bremen envoy Heinrich Oldenburg (1615-1677) together with a number of English scientists. Three years later the society received royal patronage and became known as the Royal Society. Boyle now devoted himself entirely to natural science and was president of the Royal Society from 1680 till his death in 1691.

Like Jungius, Boyle fought against alchemistic and iatrochemistic views and tried, like Bacon, to free himself from obsolete prejudices and to place chemistry and natural science generally on the foundation of experimental experience. "The chemists," he said. "view their task as the preparation of medicines and the extraction and transmutation of metals. I have tried to deal with chemistry from a quite different viewpoint, not as a physician or an alchemist but as a philosopher. If men had the progress of true science more at heart than their own interests, one could easily persuade them that they would render the greatest possible service to the world by devoting all their efforts to setting up experiments and making observations and by not proclaiming any theo-

ries without previously having tested the relevant phenomena."

Boyle thus proclaims the task of chemistry to be the experimental investigation of the properties of substances without any other subsidiary purpose. Chemistry is henceforth an independent science. Boyle was also an adherent of the corpuscular theory. The smallest "corpuscles" of the different elements differ from each other in the three basic qualities of shape, size and motion. Even in their solid state he viewed the corpuscles as in permanent motion, increasing with rising temperature. It was thus that he explained the glimmer of ground diamonds in the dark.

In his chief work, the "Sceptical Chymist" or "Chymista scepticus," of 1661, Boyle expounds his views on the nature of chemical elements. Like Jungius, he proclaims them to be simple substances that cannot be further decomposed chemically. As a "sceptical chymist" he leaves open the question of whether they might not be formed as closely put together "clusters" of 3, 4 or 5 basic elements like the "spagyric principles" or the elements of Empedocles and Aristotle. When one bears in mind the most recent results of atomic research and replaces the "principles" or "elements" by protons, neutrons, electrons, etc., one must conclude that Boyle's views are not very far from those of our own day.

Boyle was not only a distinguished theoretician but he also served chemistry by his experimental investigations. Most previous investigations of various substances were limited to observing their changes under strong heating up to glowing. He introduced observation in aqueous solution by using the precipitations and colorings produced by solutions of other substances as characteristic marks. After the first tentative experiments of Tacke and Glauber, Boyle became the real founder of analytical chemistry in the sense we use this phrase today. He also introduced the word "analysis" (really mean-

ing dissolution) to describe this kind of investigation. He established the use of certain vegetable juices (gallnut, violet, litmus) as "indicators." Like Glauber, Boyle busied himself with problems of industrial chemistry. He not only carried out fractional analyses in which he discovered methyl alcohol and acetone but also distillation under reduced pressure, i.e., so-called "vacuum distillations." He used coal as well as wood and turf for heating purposes.

The Hamburg alchemist Heinrich Brand had discovered phosphorus in 1669 by strong heating of evaporated urine and created a great sensation. It was the first new element after the discovery of zinc and bismuth and remained the only element discovered in the 17th century. Brand naturally kept his discovery a close secret and permitted others to use it only against a still fee. The great philosopher Gottfried Wilhelm Leibnitz (1646-1716) got wind of the discovery through some dubious intermediaries and made a large-scale demonstration of phosphorus by treating the urine of the entire garrison of Hannover. (Similarly, in male and female urine were collected separately on Tempelhof airfield in order to produce the newly discovered hormones.) Boyle also occupied himself with the strange new substance and he introduced improved methods of production by adding certain substances like sand and coal to the evaporated urine residue. He also observed that an acid is formed in the burning of phosphorus.

Brand's laboratory assistant Gottfried Hankewitz had for a long time the monopoly of phosphorus production, supplying all European chemists. The price for an ounce was 10 to 11 ducates in England and 16 ducates in Amsterdam (one ducate is about 2.40 dollars).

Boyle was also engaged in studying the combustion processes. He realized that in combustion, as in breathing and the calcination of metals, air is being used. Nor did the fact that, e.g., tin or lead gain weight in calcination escape him,

even though his weighings were not especially accurate. He tried to explain the increase in weight by assuming the existence of a weighable fire substance. Robert Hooke (1635-1703), who participated in these experiments, developed the counter-theory that the burned substance was absorbed in a finely divided state by a component of air that is also found in saltpeter.

Hooke also assisted Boyle in his experiments with the air pump invented in 1652 by the mayor of Magdeburg Otto Von Guericke (1602-1686), who created a great sensation at the Regensburg Reichstag of 1656 with his "Magdeburg hemispheres." Boyle was concerned with the problem of air pressure. Evangelista Torricelli (1608-1647), a pupil of Galileo, had discovered the barometer in 1643. Boyle followed his example by experimenting with U-shaped tubes. By measuring equilibrated liquid columns of water and mercury he determined the specific weight of mercury as 13.76 (instead of 13.54). By isolating a definite quantity of air in a shorter leg closed up with wax and by pouring mercury into the longer leg of the tube, he could flow up and measure the increase in the volume of air and determine the ratio between pressure and volume. He thus discovered in 1660 the natural law that the volume of a gas is inversely proportional to the pressure exercised on it— $v_1:v_2=p_2:p_1$ . The French priest (1620-1684) Edme Mariotte made the same discovery independently 16 years later, hence the name "Boyle-Mariotte law."

Another testimony to the variety of Boyle's talents is the fact that he was the first man to carry out a blood transfusion, between two dogs. In spite of his clear definition of the concept of element he was not entirely opposed to alchemistic attempts to transmute metals. He was and remained a skeptic: he confessed that other peoples' theories were hardly less satisfactory to him than his own. In addition to



the "Sceptical chymist," he wrote a number of other books and he reported on his work in the "Philosophical Transactions" of the Royal Society.

## *2. Other Important Chemists of the 17th Century*

One of the most important German chemists of the 17th century was Johannes Kunckel (1630-1702).

He was born at Huetten near Rendsburg as son of the court chemist and alchemist of the Duke of Holstein. He followed his father's profession in the service of a number of German rulers and, probably like all the other chemists of his time, still held alchemistic views, even if he rejected some of the alchemistic concepts like the "alkahest" and the "potable gold." For a brief period (1677-1679) he taught experimental chemistry at Wittenberg University; then the Grand Elector Frederick William called him to Berlin, to exercise his alchemistic art with the title of "secret aulic councilor" (*Geheimer Kammerdiener*).

He received a fully equipped laboratory on Peacock Island near Potsdam, where he worked undisturbed for years. Brand's discovery turned his mind to the production of phosphorus and he managed to extract that wonderful element from bones. The production of glass was among his main preoccupations. He built big smelting furnaces and, like Glauber a few years before him, he managed to produce ruby glass with the aid of gold, though he did not produce gold itself. He also manufactured lead glass, smelts and artificial jewels. He wrote a book on the "Perfect Glass-making," partly based on "The Art of Glassmaking" of the Florentine abbé Antonio Neri (1612). Kunckel's manual appeared in 1678/89 and was used for a considerable time. It was re-issued at Nuremberg as late as 1756.

When his princely patron died on May 9, 1688, Kunckel

had to leave. His smelting furnaces and other installations on Peacock Island were destroyed by malicious enemies. He first withdrew to a property he acquired in Brandenburg and then to Sweden. He worked there as a chemist for a considerable time and was ennobled by King Charles XI with the title of "Kunckel von Loewenstern."

The physician and pharmacist Nicholas Lemery (1645-1715) influenced the development of chemistry in France.

He gave public lectures on chemistry in Paris for several years. Though persecuted as a Protestant, he refused an invitation from the Great Elector to come to Berlin. Finally, after a stay in London, he returned to Paris, yielded to pressure and became a Catholic. He was an adherent of the corpuscular theory and developed phantastic hypotheses about the form of the smallest particles to visualize their solid cohesion by mechanical devices like hooks and eyes. Like Boyle, he explained the elasticity of air by attributing to the air corpuscles a spiral form, like that of wool fibers. Men of his time could think only in mechanical concepts. It is enough to recall that Newton's "Principia," with their general theory of gravitation, did not appear until 1687. Lemery rendered great services to chemistry as a systematizer: he was the first to subdivide chemistry into mineral, vegetable and animal. His "Chemistry Course" of 1675 was the first adequate textbook of chemistry. It was translated into a number of languages, including Latin; an Italian edition appeared as late as 1763.

The German Wilhelm Homberg (1652-1715) was another chemist active in Paris at the time.

He was born at Batavia where his German father worked as a Dutch colonial official. He was a lawyer at first and practiced at Magdeburg, where he turned to natural science and medicine under the influence of Otto von Guericke. After some adventurous years in Germany, Italy, France

and England (he was working in Boyle's laboratory for a time), he finally settled in Paris in 1691. He became personal physician to the Duke of Orleans and, like Lemery, had to become a Catholic.

Homburg can be credited with considerable chemical achievements. He obtained phosphorescent stones (Homburg's pyrophores) by carbonizing alum with sugar; he produced alloys with a low melting point from lead, bismuth and tin and extracted boric acid from borax, though he did not recognize its acid character ("Homburg's sedative salt"). By determining the quantities of various acids required to neutralize a given quantity of base, he made the first stoichiometric experiments. He still adhered to Paracelsus' "three principles" and ascribed to sulfur a part similar to the later phlogiston.

Johann Joachim Becher (1635-1682) was another man active in those troubled times. His many-sided talents and astonishing drive put him in advance of his contemporaries and his theoretical views were particularly important to the later development of chemistry.

He was born at Speyer, son of a Lutheran pastor from Wittenberg. Orphaned at an early age, he had to earn the means necessary for studying. He became a doctor of medicine at Mainz University, taught there and became personal physician to the archbishop-elect. He moved to Munich to become personal physician to the Elector of Bavaria; but could not stay there for long. His life was adventurous and his occupations varied. He worked out all kinds of plans—for a Rhine-Danube canal, colonies, a world language, industrial enterprises. He worked as diplomat for a number of German rulers, including the emperor. After short stays in Vienna, Holland and other places he moved in 1680 to England, where he busied himself with coal mining and the industrial exploitation of coal. He is the real founder of the

coal tar and gas industries and was the first to use coal gas for lighting purposes, as "philosophical light." It was over 100 years until similar experiments were made by others: professor Minkellers of Louvain and professor Bickel of Wurzburg lit their lecture rooms and laboratories with gas about 1785. Another important forerunner was Wilhelm August Lampadius (1772-1842), professor of the Mining Academy at Freiberg in Saxony, who lit part of the town with gas in 1811. Gas lighting became common in England in the beginning of the 19th century and soon spread to the larger cities of Germany: Hannover was lit by gas in 1825 and Berlin in 1826.

Becher's life was split and shortened by his astonishingly varied talents: he died at 47 and is buried in St. James' church in London. He wrote a number of books, including one entitled "Foolish wisdom and wise foolishness." While at Munich he published in 1699 a book that had an extraordinary importance on the future growth of chemistry: "Acts of the Munich chemical laboratory or Subterranean physics." (It was reprinted under the latter part of the title.) He varied Paracelsus' "tria prima" into a "theory of the three earths," the *terra fusilis*, *terra pinguis* and *terra mercurialis*, the three being different forms of the same primary earth (*Uierde*) and being the components of all bodies. Of special importance is *terra pinguis*, the fat earth, which is contained in all inflammable or calcinable substances and escapes in heating or with the flame. Becher further developed his views in his last work, the "Mineral alphabet or 24 chemical theses" (1682). He laid the foundations of the phlogiston theory.

### *3. Age of the Phlogiston Theory.*

The phlogiston theory was then developed in detail by

Georg Ernst Stahl (1660-1734). He was born at Ansbach, studied medicine at Jena and taught there at 23. In 1687 he became personal physician to the Duke of Sachsen-Weimar.

When Halle University was founded in 1693, he was called there as second full professor of medicine, in charge of the so-called "institutions" (physiology, pathology, dietetics, pharmacology and botany). After a successful academic career of 23 years he went to Berlin in 1716 to become personal physician to King Frederick William I of Prussia. He remained there until his death. He freed himself from obsolete alchemical notions and became, beyond doubt, the first chemist of his time, while enjoying great fame as physician. Unlike the iatrochemists, he kept these two sciences strictly separate. His "True medical theory" (1708) proclaimed the "animist" view, which held that the soul was the true bearer of all life phenomena. He also adhered to the Pietist variety of Lutheranism, founded by P. J. Spener (1635-1705) and successfully represented at Halle by August Hermann Francke (1663-1727).

In his chemical experiments Stahl tried to solve the problem of the chemical affinity between the bases and metallic oxides on the one hand and sulfur and acids on the other. He considered the formation of precipitations in aqueous solutions to be particularly important in determining the degree of affinity. He investigated different strengths of acids and recognized that the "alkaline component" of potash is different from that of common salt and that alum contained a special earthy component. He also made other chemical experiments but he believed that his main task was to find an adequate theoretical explanation of such phenomena as combustion, calcination of metals, breathing, etc. He thought that Becher's theory provided such an explanation ("I prefer Becher's views" he used to say in his lectures which, as was customary at the time, he gave in Latin).

Becher's "fat earth" became Stahl's "phlogiston" ("combustible," from the Greek "phlox," flame). Van Helmont had already used this word in a similar sense. Phlogiston was supposed to be contained in all substances that are combustible or can be changed by heating and to vanish in the calcination of metals and in the burning of organic substances through a flame. It was also supposed to play a decisive part in respiration, fermentation and decomposition. The residues of substances remaining after phlogiston had been given off could be in many cases changed back to their original state by adding phlogiston to them. Thus, calcinated metals turn once more to metals when heated with coal, which is almost pure phlogiston. sulfuric acid to sulfur and so on.

The phlogiston theory, developed in total negligence of the weight ratios—even though Stahl and other chemists of his day were familiar with the increase in the weight of metals in calcination—found quickly a general acceptance. Kant wrote in his "Critique of pure reason" as late as 1787: "Stahl's phlogiston theory was like a light to natural scientists." The concepts of matter, mass and weight were still very hazy to men of Stahl's time.

Stahl left some 200 writings, of which the most important are the "Fundamental zymotechny or general theory of fermentation" (Halle, 1687) and the "Accidental thoughts and useful hesitations on the quarrel over the so-called sulfur" (1718). Both these books expound his phlogiston theory. In 1702 Stahl re-issued Becher's "Subterranean physics," published in 1669. Stahl called it "a book without its equal, first and foremost up to now" and added to it his own appendix, called "Fundamental Becherian specimen consisting of documents and experiments." Stahl's lectures were frequently published, independently from his, in the form of student notes and under titles like "Basic chemistry and

pharmaceutics." His pupil Johann Juncker (1683-1759) published in 1737 a "Conspectus of theoretical and practical chemistry." It was translated into French in 1757 by J. F. Demachy (1728-1803) and did much to spread the phlogiston theory in France.

Friedrich Hoffmann (1660-1742), son of the Halle municipal physician, was a contemporary and colleague of Stahl.

Left to his own devices by the early death of his parents, he nonetheless acquired a thorough education and studied medicine at Jena at the same time as Stahl. He made a study trip to Holland and England, where he met men like Sydenham and Boyle. He then became medical officer to the city and garrison at Minden and later at Halberstadt. In 1693 he became professor at the newly established Halle University, where he taught the "practical" subjects (anatomy, physics, chemistry). He came into conflict with his colleague Stahl, whom he had caused to come to Halle, because his mechanistic and dynamistic views clashed with Stahl's "animism." His academic career at Halle was broken by a spell as personal physician to King Frederick I of Prussia (1709-1712). Frederick's successor Frederick William I also consulted him medically after Stahl's death.

Hoffmann was specially interested in mineral waters, this interest having been roused during his stay at Minden through the neighboring spa, Bad Pyrmont. He also analyzed the waters of another spa, Lauchstaedt near Halle. His textbook, "Method of examining medicinal waters" (1703) offers procedures for tracing carbon dioxide and other components of mineral springs. He was the first to create, on the basis of chemical analysis, the classifications of alkaline, salt, bitter, ferrous and sulfuric waters. He also proved that the belief that certain waters contained gold and silver was erroneous. Hoffmann also made mineralogical and geologi-

cal studies, with special reference to different crystal forms. He was only a limited adherent of Stahl's phlogiston theory. Hoffmann held that the reduction of metals from their "calxes" (oxydon) did not occur through absorption of phlogiston but through the separation of a special substance, the "sal acidum" (acid salt, oxygen). Unfortunately, Hoffmann did not pursue this correct trend of thought but, like Stahl, he turned his own view into a general theory. His "Complete physical and chemical works" were published in 1742; his detailed textbook "Rational and experimental chemistry" only after his death, in 1748. The "Hoffmann Drops" (Liquor anodinus Hoffmanni or Spiritus aethereus) keep his name alive in medicine and pharmaceutics. When a "treasure secker" mysteriously died at a garden pavilion in 1726 Hoffmann proved that his death was caused not by the devil but by the poisonous effects of coal gases.

Herman Boerhaave (1664-1734) did for chemistry in Holland what the two Halle professors did in Germany.

He was born at Voerhout near Leyden, the son of a minister. Early orphaned, like Hoffmann, he had obtained by tutoring the money required for his education. He studied medicine and the natural sciences at the small university of Hardewijk (abolished in 1811), and became a doctor in both medicine and philosophy. He first practiced as physician; in 1701 he became lecturer in medicine at Leyden, becoming professor of medicine and botanics in the following year. To this was joined in 1709 a professorship in chemistry, a subject that was Boerhaave's special interest. ("He practiced chemistry by day and by night," he wrote in an autobiography.) In addition to his several professorships he had a lucrative and distinguished medical practice. He became a European celebrity and had trouble in dealing with his vast correspondence. His fame spread to the ends of the earth and letters reached him addressed to "Mr.



Boerhaave, physician, Europe." But though he had a large income and left his only daughter 2 million guilders he led a modest and simple life, devoted to uninterrupted medical and scientific activities. Boerhaave remained true to his motto of "Simplicity is the seal of truth."

Boerhaave tried to free chemistry, which he kept strictly separate from medicine, from the still very prevalent alchemist views. By heating a sample of mercury uninterruptedly for 15 years and distilling another no less than 500 times he experimentally disproved the traditional view that it was possible to transform mercury this way into a solid metal or a more volatile substance. He also proved that it was impossible to turn lead by special treatment into mercury by performing the experiment strictly according to the prescribed procedure. He accepted the phlogiston theory but he suspected that air contained a "food of life" and thought that one of chemistry's most important tasks was to investigate it. He said that "it is still in the dark and happy is he who shall bring it to light," forecasting the discovery of oxygen some 50 years later.

Boerhaave's contribution to chemistry lies less in his new observations and discoveries than in his clear and systematic treatment of existing knowledge and his eminently successful teaching. When some of his students published his lectures without his knowledge but under his name as "Chemical institutions and experiments" (1729) this normally very calm and self-controlled man became exceedingly angry, especially since the text contained errors. But his violent protest in a Leyden newspaper against this abuse merely resulted in French and English translations of the illegitimate Latin text.

Boerhaave was thus forced to write his own textbook, the "Elements of Chemistry" of 1732. It was soon translated into German, French and English and spread all over

Europe. It was clearly written and systematically arranged and offered an excellent general survey.

The phlogiston theory was further developed in Germany by the "Berlin school," founded by Stahl. Its chief exponent was Caspar Neumann (1683-1737), court apothecary and professor at the College of Medicine and Surgery. His chemical investigations were specially concerned with vegetable oils. He observed the precipitation of stearoptenes and extracted a volatile oil through the distillation of ants. But his chief contribution was through his teaching by both the written and the spoken word. He published several papers in the Proceedings of the Berlin Academy and the Philosophical Transactions of the London Royal Society. His lectures on various branches of chemistry were collected and published after his death as "Chemical Lectures" in 1740. Dutch, French and English translations followed.

Johann Theodor Eller (1689-1760), professor of anatomy at the military college where Neumann taught and head of the physical and mathematical section of the Berlin Academy, also lectured on chemistry. He was personal physician to Frederick the Great. Johann Heinrich Pott (1692-1777), a pupil of Stahl and Hoffmann, became a knowledgeable chemist and a skillful experimenter. He took over Neumann's chair after his death.

Pott was an ardent adherent of Stahl and held phlogiston to be a special kind of sulfur. He was particularly concerned with minerals which he exposed to very high temperatures in specially improved furnaces. Frederick the Great asked him to imitate the Meissen porcelain, whose discovery had created a great sensation. With admirable persistence Pott made some 30,000 experiments with all possible materials: he did not achieve his aim because he could not lay his hands on the porcelain clay, kaolin. The results of his experiments proved useful in later porcelain manufacture and

may be considered precursors of blow-pipe analysis. Pott published his papers in the Transactions of the Berlin Academy and in book form. He polemicized with Eller, especially over the old question of transforming earth into water—Pott tried to prove experimentally that this was impossible. His "Collection of chemical observations and controversies" (1739/41) contains detailed data about the qualities of metals like zinc and bismuth.

The discovery of porcelain marked one of the greatest technical advances of that era. Like so many others, it was achieved as a by-product—one might almost say as a "fear product"—of alchemistic endeavors. Objects made from the baked white shimmery paste could be only obtained at great expense from distant China. All attempts to produce them in Europe failed. But in 1709 Johann Friedrich Boettger (1682-1709) succeeded. He was a pharmacy apprentice from Schleiz, whose alchemistic experiments in Zorn's pharmacy in Berlin earned him the reputation of a skilled goldmaker. He was employed as such even by King Frederick I of Prussia.

But Berlin became too hot to hold him and, like Thurneysen in 1584, he fled in 1701 to Wittenberg, then belonging to the Electorate of Saxony. Prussia put a price of 1000 Talers on his head and almost went to war with Saxony over him when negotiations for his return failed. Augustus the Strong of Saxony had Boettger seized at Wittenberg and taken to the fortress of Koenigstein near his capital Dresden. There Boettger was kept under strict surveillance and was supposed to produce gold for the splendor-loving and money-needing ruler. He tried to escape, was caught and assigned to work as assistant to famous physicist Ehrenfried Walter von Tschirnhaus (1651-1708) in Dresden itself. Tschirnhaus had busied himself with glassmaking and had also tried to produce porcelain. He made study trips to Italy,

Holland and France and had learned in Paris to produce high temperatures by using burning reflectors. He finally succeeded in making vessels of brown porcelain but death interrupted his experiments in 1708.

Boettger, who realizing the hopelessness of his alchemistic experiments had become an eager assistant to the distinguished scientist, succeeded in obtaining genuine white porcelain shortly after his master's death. For white kaolin had been found in the meantime and, mixed with feldspar, it gave the proper paste. The porcelain factory of Meissen was opened on June 7, 1710. Boettger headed it for only nine years more. The secret, however strictly guarded, could not be kept. Porcelain factories were set up at Vienna (1720), Hoechst (1740), Fuerstenberg (1744) and Nymphenburg (1747). Prussia had started one as early as 1713 at Plaue near Potsdam; it did not stay open long because it made only red stoneware. Only when the secret of making the proper paste from kaolin and feldspar penetrated to Prussia could a factory be started in Berlin (1751).

The most important of Neumann's pupils in Berlin was Andreas Sigismund Markgrafe (1709-1782; the name is usually spelled "Markgraf" but he invariably signed himself with an "e").

He followed in his father's footsteps as court apothecary and got his first education from him while Neumann was responsible for his further chemical education. He went on to study at the universities of Frankfurt on the Oder, Strasbourg and Halle and the Mining Academy of Freiburg. He completed this thorough education by studying mining and foundry work on the spot, and returned to Berlin. At the early age of 29 he became head of the chemical laboratory of the court pharmacy and member of the Royal Society of Sciences of Prussia. The latter put at his disposal a house with a chemical laboratory attached (at Number 10, Doro-

theenstrasse). After Eller's death, Frederick the Great named him head of the physical and mathematical section of the Academy, a post which he kept till his death.

Markgrafe was a serious and eager investigator. He avoided controversies and he modestly and generously recognized the achievements of others. He developed the concept of analytical chemistry started by Boyle. While, e.g., already Hoffmann suspected that alum, lime and magnesia contained different "earths" but was unable to indicate their differing characteristics, Markgrafe taught how each of them could be traced by definite reactions. He proved that gypsum contained lime, sulfuric acid and water. He used differing flame colors to distinguish between sodium and potassium salts.

Antonio de Ulloa, a Spanish scientist who had taken part in a French expedition to determine the length of a degree, reported in 1748 the presence of an "impalpable metallic stone" in the equatorial region. The Englishman Richard Watson recognized it as a new metal in 1750 and H. T. Scheffler (1710-1755) examined its properties more closely at Upsala in 1752. The Spaniards believed it to be an inferior kind of silver and called it "platina del Pinto" (little silver of the Pinto River near which it was first found). It was only gradually that men realized the true importance and value of this precious metal.

Markgrafe managed to obtain some platinum and used its solution in aqua regia (platinum chloride) as a chemical reagent to separate sodium salts from potassium salts (1757). He improved the method of extracting phosphorus from urine and found that the weight of phosphorus increased with combustion. He examined the properties of phosphoric acid and its salts and introduced microcosmic salt (sodium ammonium phosphate) into chemistry. While he made many more investigations, there were a number of cases—with manganese dioxide, fluorspar and heavy spar

—where he failed to get results later obtained by greater minds than his.

One of Markgrafe's signal achievements was to introduce into the chemical laboratory the microscope, invented by the Dutch lensgrinders Johannes and Zacharias Janssen in 1590. With its aid he was able to discover in 1747 the presence of cane sugar in beets. But he made no attempt to put his important discovery to practical use. His disciple and successor Franz Carl Achard (1753-1821) built a small sugar factory at Karlsdorf near Berlin in 1786; but it burned down before it was put to use. In 1799 he started a new factory on his property of Cunern near Breslau, which he acquired with the aid of King Frederick William III of Prussia. After overcoming great initial difficulties he succeeded in obtaining cane sugar industrially in marketable quantities. The undertaking flourished during Napoleon's Continental Blockade and Achard was granted a gold medal in 1810 by the "Societe d'Agriculture de la Seine." But when British colonial sugar flooded the country following the end of the blockade the factory had to be closed. But industrial production of beet sugar was further developed in France. Achard—who, incidentally, produced the platinum crucible in 1784—died in great poverty. After his death the beet sugar industry flourished in Germany and other European countries. The sugar content of the beets was increased by breeding special varieties and industrial methods were greatly improved.

Markgrafe wrote his chemical treatises in German. They were translated into Latin for the "Berlin Miscellanies" and then from Latin into French for publication in the "History of the Royal Academy of Sciences and Letters." The first volume of his "Chemical writings" was published in 1760 by Johann Gottlieb Lehmann (died 1767), Prussian mining councilor and later chemistry professor at Saint Petersburg.

The Seven Years War delayed the publication of the second volume till 1767. Markgrafe suffered a stroke in 1774; after the king had had no news from him for some time he assumed that Markgrafe was dead and named his successor. The chemist was also ignorant about his remuneration. The professors of the Academy reported to the king that "Director Markgrafe is not dead; he is not only alive but works as hard as ever. He never earned 1600 Talers but only 900, including his director's salary." He sold his laboratory equipment, which he had acquired at his own cost, to the Prussian Treasury, which recovered its solvency after the end of the Seven Years War. Markgrafe asked only 300 Talers for his equipment, although its value had been estimated at 322.

A number of French chemists attacked and defended the phlogiston theory. Among them was Stephan François Geoffroy (1672-1731, called the Elder to distinguish him from his brother Claude Joseph, 1686-1752), who was physician and pharmacist as well as chemist. He further developed Stahl's idea of chemical affinity of different elements; he composed Affinity Tables arranged according to the formation of precipitations in the solutions of the various salts. His "Tables des rapports," published in 1718, played for a long time an important part in chemistry and produced a number of improvements and additions to the chemical systems. Geoffroy and other French chemists were active in Paris, where the University and a number of other scientific institutions offered them good opportunities.

Among them was Jean Hellot (1685-1765) active in industrial chemistry, especially in dyeing and agriculture (potato cultivation). Henry Louis Duhamel de Monceau (1700-1781) especially investigated alkalis. He proved that the alkaline nature of the base contained in common salt was the same as that of "natron" or "throna," found in

Egypt in natural state, and of "soda," produced by ashing shore plants, especially in Spain; but it was different from "potash," produced from inland plants.

Duhamel also made in 1736 the first attempt to manufacture soda, though he failed to obtain a practicable procedure. After other chemists tried their hand at it, Nicolas Leblanc (1742-1806), personal physician to the Duke of Orleans, succeeded. He first turned common salt into Glauber's salt by treating it with sulfuric acid; then obtained soda from Glauber's salt by heating it with coal and chalk. Michel Jean Jerome Dize (1764-1852) helped him to work out the industrial processes. The patent granted for this method on September 25, 1791 was withdrawn by the revolutionary government in 1794. Leblanc, the founder of the soda industry, was ruined. After years of bitter poverty he shot himself in a poorhouse at Saint Denis.

Other French chemists of that time include Guillaume Francois Rouelle (1703-1770), an excellent theoretician and a successful teacher. He trained Leblanc and Lavoisier. He was the first to clarify finally the concept of "salt" and to make the subdivisions into neutral acids and base salts. Pierre Joseph Macquer (1718-1784) was an industrial chemist, especially useful in dyeing and the manufacture of porcelain. He occupied himself with the "Berlin" or "Prussian" Blue, obtained at the beginning of the 18th century by the Berlin dyeing expert Diesbach, who used the alkaline waste material with which the theosophist and alchemist Johann Conrad Dippel (1673-1734) cleaned his "Dippel's animal oil." Its first description appeared in the "Berlin Miscellanies" of 1710. Macquer also wrote some excellent textbooks: "Elements of theoretical chemistry" (1749); "Elements of practical chemistry" (1751) and "Chemical dictionary" (1766).

English chemistry also produced some important men in



the 18th century, especially Joseph Black (1728-1799).

Black was born at Bordeaux (his father was a wine merchant from Belfast) and studied medicine at Glasgow and Edinburgh. His interest in chemistry was roused by the excellent Glasgow lectures of William Cullen (1712-1790). He started making his own experiments for his medical dissertation which dealt with the healing of bladder stones by the application of caustic waters. A treatise by Hoffmann got him interested in magnesia alba obtained by mixing a hot solution of Epsom salt (magnesium sulfate, obtained from the waters of Epsom spa, Southwest of London) with a hot potash solution. Black gained his doctorate at Edinburgh in 1754 with a thesis on "Acidity arising from food and magnesia alba."

After supplementing his dissertation by further investigation he published it in 1755 under the title "Experiments upon magnesia alba, quicklime and other alkaline substances." This work, dedicated to his teacher Cullen, was the basis of his high reputation as a scientist. By 1756 he became Cullen's successor at Glasgow and he took over Cullen's chair of chemistry at Edinburgh in 1766 when Cullen exchanged it for the chair of medicine. Black's other scientific achievement is his discovery of latent heat, published in 1775 in the "Philosophical Transactions" after special urgings. Generally speaking, Black published little; he expounded all his knowledge and powers in his lectures, published later on by his students. His lectures inspired James Watt (1736-1819) to construct his steam condenser, a decisive step in the development of the steam engine. One proof of Black's high reputation among his fellow scientists was his election as foreign member of the French Academy of Scientists, an honor granted to only eight foreign scientists.

Chemistry owes to Black the distinction between "mild" and "caustic" alkalis. It had been hitherto assumed that

limestone absorbed in combustion a cauterizing caloric; Black showed that, on the contrary, the "fixed air" is expelled and that the burned lime again cauterizes the mild alkalis by taking over the carbonic acid bound in them. Black was also the first to weigh the "fixed air" and to prove that it was contained, in small quantity, in the atmosphere.

The educational effect of Black's basic investigations was held up for a time by the strange theory of the Osnabruck pharmacist Johann Friedrich Meyer, published in 1764. He derived "causticity" from a "fatty acid" originating in fire. This variety of the phlogiston theory divided the scientific world into "Blackians" and "Meycrians;" the controversy ended only in the 1770's with the general triumph of Black's view.

No less important than Black was Henry Cavendish (1731-1810) who came, like Boyle, from a distinguished family of the English aristocracy. Cavendish, who never occupied any public position, devoted his life to science.

Cavendish, son of the second Duke of Devonshire, was born at Nice, where his mother stayed for reasons of health. He went to school at Hackney and then studied mathematics and the natural sciences at Cambridge. But after several years he moved to London without taking his final examination. He set up a laboratory in the family's town house and became a member of the Royal Society. He was eccentric, shy and withdrawn, and led a modest and retiring life. He was solely devoted to scientific investigations and made no use of the very considerable wealth which he inherited after the death of his father and some close relatives. He installed a large library which he opened up to his friends and from which he took out books only against a receipt that others also had to sign. He had a simple country house in the suburb of Clapham where he spent the summer. In order not to interrupt his investigations he had another

laboratory installed there. Special friends who visited him there were regularly fed on a leg of lamb. When one of his former employees, the father of a family, needed money and Cavendish was asked to make a contribution, he wrote out a check for 10,000 pounds and asked if this was enough. He remained a lonely bachelor to the end of his days and an obituary said that he was the richest of scientists and the most scientific of the rich.

Cavendish's scientific work was marked by the fact that he was a physicist and a mathematician as well as a chemist. Unlike most of the other chemists of the phlogiston era he was a quantitative scientist working with weight, measure and number. Like Black, he discovered the latent melting and evaporation heat, without publishing his discovery. They share the glory of the discovery with a third man, the German-Swedish chemist J. C. Wilcke (1732-1796). Cavendish also cleared up the concept of specific heat and determined it for a considerable number of substances. He explained the mysterious phenomenon of shocks by electric eels by discharges of high electric voltages. His most important achievement in physics was to determine the gravitation constant with a lead ball torsion balance, generally referred to as "determination of the weight of the earth."

One of Cavendish's first chemical investigations, whose results remained unpublished as in many others, concerned metallic arsenic and its two oxides. It was then believed that the pentoxide contained less phlogiston than the trioxide while arsenic regulus was richest in it. Cavendish determined the solubility of magnesium and calcium carbonate under the action of excess carbonic acid (formation of carbon dioxide). Like Homberg he attempted, with his quantitative methods, some stoichiometric determinations. He determined the quantity of "vitriol oil" (sulfuric acid) required on the one hand to produce 100 weight parts of lead vitriol and on the other to

dissolve 33 weight parts of marble. He found that this quantity of vitriol oil saturates as much "fixed alkali" as the weight part of nitric acid that can dissolve 33 weight parts of marble. Cavendish established this rule before the concept of equivalence was developed by J. B. Richter (1792) and that of atomic proportions by J. Dalton (1803). Cavendish's ratio of 33:1 corresponds exactly to that of  $\text{PbSO}_4$  (303.23) :  $\text{CaCO}_3$  (100.08).

Cavendish's special interest and greatest achievement was in the chemistry and physics of gases. The chemistry of gases was founded by Van Helmont and developed by Boyle and Black. The great difficulties encountered in the investigation of various "kinds of air" were substantially overcome by the invention of the "pneumatic bath" in 1727 by the English country parson Stephen Hales (1677-1761). Cavendish, too, used this appliance to receive the different gases separately and to study their mutual relations. He used mercury as sealing liquid instead of water to avoid absorption. He reports on his investigations in his "Experiments on factitious air," published in 1766. (This was his first publication.) Like Paracelsus, Van Helmont, Boyle and others before him he was concerned not only with the "gas sylvester" or "fixed air" (carbon dioxide) but also with "inflammable air" (hydrogen), developed with dissolution of metals in acids. Cavendish determined the density of these gases in different ways (weighing in animal bladders, determining the loss of weight of inter-reacting quantities of metal and acid). He found that if the density of air is equal to 1, that of carbon dioxide is 1.57 and that of hydrogen 0.09 (instead of 1.59 and 0.069). This same "inflammable air" was developed with different metals and acids and Cavendish, oddly enough, noted that when mixed with air and set aflame it always had the same strength of detonation. These exact investigations of Cavendish characterized hydrogen for the first time as an independ-

ent gas; Cavendish thus "discovered" hydrogen. Since the "fixed air" is expelled from magnesia or marble by the acids, it was all too easy to assume that "inflammable air" was developed from metals under the action of acids and was therefore nothing but the famous but impalpable phlogiston. Cavendish himself later on viewed hydrogen not as pure phlogiston but as "phlogiston hydrate." This phlogiston-hydrogen theory was later proclaimed by the Englishman Richard Kirwan (1750-1812) and the German Johann Chr. Wiegleb (1732-1800) of Langensalza.

After an interval of 17 years Cavendish decided in 1783 to publish a new "pneumatic" treatise. "An account of a new eudiometer." Several important discoveries in gas chemistry had meanwhile been made in the early 1770's. Cavendish himself, as he reported to Priestley in a letter (1772), had found a gas that extinguished a flame and was slightly lighter than air by passing air over incandescent wood charcoal and caustic potash. He called it, to distinguish it from "fixed air," "phlogistics" or "mephitic" air (from Mephtis, old Italian goddess of noxious exhalations). But since, as usual, he was in no hurry to publish his results, the glory of discovering nitrogen fell to Daniel Rutherford (1749-1819) who published in the same year his inaugural dissertation "On fixed or mephitic air" for Black.

The discovery of oxygen by Scheele and Priestley (1771 and 1774) finally proved that air is composed of two different gases. Cavendish now set himself the task to determine exactly these two components of air by using the property of "salt-peter gas" (nitric oxide) to combine with the "dephlogisticised" component of air under formation of a reddish-brown color to make quantitative determinations through absorption in water. Stephen Hales, the discoverer of the pneumatic bath, had also made a eudiometer, an instrument to measure the "goodness" of air. Cavendish made the method still more

exact and made extensive investigations in various places to find out whether, as was believed at the time, air was composed differently at different times and in different places. From over 400 individual experiments he concluded that the composition of the air remained the same everywhere and in all weathers; after eliminating "fixed air" there was a mean 20.84% of "dephlogisticised" air (oxygen). In his "Experiments on air," published in 1784/8, Cavendish reported on his detailed experiments on the question of what happened to the "dephlogisticised" air that disappears in combustion. He found that "fixed air" was formed only in the burning of vegetable and animal substances but not in the burning of sulfur and phosphorus, any more than nitric acid. He conducted the experiments very simply by striking sparks with an electrical machine in air contained in a bent tube whose two open ends were standing in mercury. He also proved on this occasion that nitric acid (as we call it today) was composed of nitrogen, oxygen and hydrogen.

To prove whether the whole "phlogisticised" air component (nitrogen) could be converted into nitric acid, he treated a definite quantity of air with excess "dephlogisticised" air (oxygen) with electric sparks until there was no decrease in volume. After he had eliminated the excess oxygen with the aid of hepars, there remained a small residue of gas, about 1/120 of the "phlogisticised" air used. For over a century this finding of the exact scientific worker Cavendish remained strangely unnoticed, although such excellent physicists and chemists as Gay-Lussac and Bunsen were intensely busy with the analysis of air. It was only in 1894 that argon was discovered by John William Lord Rayleigh (1842-1919) and William Ramsay (1852-1916), using instruments not available to Cavendish. One more example how an early discovery was completed late.

Cavendish was inspired by Warrington's communication to

Priestley in 1781 on the appearance of humidity in the explosion of a mixture of "inflammable" and ordinary air to carry out a thorough experimental investigation of this question. By using a large glass tube (8 feet long and  $\frac{7}{8}$  of an inch in diameter) he succeeded in obtaining 135 grains (8.7 grams) of water that had neither smell nor taste and left no residue in evaporation. Cavendish thus proved—as he put it himself—that "dephlogisticised" air consisted of water from which phlogiston had been eliminated or—actually—that water is composed of hydrogen and oxygen. James Watt, consulted by Priestley on this question, answered in the same sense. In accordance with his quantitative method Cavendish determined also the inter-reacting quantities of gases, thus forecasting the law of the volumes of gases discovered two decades later (1805) by Gay-Lussac and Alexander von Humboldt. He found that 423 measures of hydrogen needed almost exactly 1000 measures of air (corresponding to about 210 measures of oxygen) for combustion. This finding is surprisingly exact. This synthesis of water, which put an end to the traditional belief derived from antiquity that water was an element, was later completed by electrolytic decomposition of water into oxygen and hydrogen, performed in 1789 by frictional and in 1800 by galvanic electricity.

A man of very different kind who also did great work in the chemistry of gases was Joseph Priestley (1733-1804). He was born in modest circumstances: his father was a cloth-maker at Fieldhead near Leeds in Yorkshire. After the early death of his mother he was brought up by relatives and at first destined for a merchant's career.

As he quite early gave evidence of very great talent—especially for languages—and of religious interests, he went to the Daventry Academy. There he studied theology, philosophy and philology and eagerly attended lectures on the natural sciences, particularly physics. In addition to the modern

and classical languages he learned Hebrew, Chaldean, Arabic, Syriac, etc. With this variety of interests he showed a one-sided intolerance in religious matters in an outspoken opposition to the established Anglican church. He was a fanatic of religious free-thought who could tolerate no ideas besides his own. Since he was also a brave and doughty fighter he could not remain for long at peace with his surroundings. He frequently changed not only his residence and position but also—permitted by his many gifts—his profession. He hardly stuck it out anywhere for more than six years or so. Once when he managed to stay beyond that term apparently fixed for him by nature, a raging mob set fire to the roof over his head and he barely escaped with his life. That happened in 1791 when he was a minister at Birmingham. But despite his agitated life he rendered great services to chemistry. He worked as dissenting minister, language tutor, private secretary, travelling accompanist (1773-1780) and again as minister. Finally, having broken with one and all, he emigrated to America in 1794. He refused the offer of a professorship at the University of Philadelphia and spent ten years as a farmer in the area of the sources of the Susquehanna. There he died at 71, apparently the victim of a poisoning: but it is by no means certain that his wild life ended that way.

We can deal here only with Priestley's chemical work which forms but a small part of his scientific endeavors and publications. Thus he wrote a dissertation on the history of the theory of electricity which earned him, strangely enough, a law doctorate at Edinburgh. To chemistry he came comparatively late. He was led to it by lectures of a Doctor Turner of Liverpool. This happened at Warrington when Priestley was language teacher at the local academy (1761-1767). After the usual six years he became a minister, this time at Leeds, and he was able to observe in a brewery the development of gas in fermentation. This started his interest in gases which



he indulged as pure amateur, without professional training, apparently in the leisure hours left to him by his varied occupations. It was in line with his character that he did not occupy himself with a few gases, like Black and Cavendish, but with as many as possible. Half a dozen new gases were thus discovered by him, or at least traced and closely characterized. Like Cavendish, though probably independently from him, he used mercury as sealing fluid in the pneumatic bath, so that he could study in detail even gases that are easily absorbed by water.

Priestley's first experiments with gases, made at Leeds in 1767, dealt with the electrical conductivity of atmospheric, "inflammable" and "fixed" air. He manufactured sparkling mineral waters with "fixed" air. He then turned to a "nitrous" gas, nitric oxide, whose brown coloration by air had been noted a century earlier by John Mayow and which had been used by Cavendish. Priestley used this gas to determine the "goodness" of air. He did this before Cavendish but—with his qualitative outlook—he never reached Cavendish's accuracy. He was satisfied with finding that anything from one fifth to one quarter of the quantity of air was removed by the nitrous gas. But he produced, by the action of wet iron filings, a new kind of gas, in which a light could surprisingly burn—nitrous oxide. He made other experiments with air. He determined that fixed air regained by the action of green plants in daylight the capacity to sustain combustion and respiration. But his greatest achievement was the discovery of oxygen though, indeed, a few years after Scheele.

Priestley could continue with his experiments while working as librarian and secretary for the Earl of Shelburne (later the Marquis of Lansdowne), with whom he managed to stick it out for seven years (1773-1780). On August 1, 1774, he proved that when "mercurius precipitatus per se" (red mercury oxide) was heated, a gas developed that was insoluble

in water, made a candle burn much more brightly and set a glimmering taper aflame. There was no coloration and no decrease of volume in mixing it with atmospheric air, while the nitric gas produced a reddish brown coloration. This "dephlogisticised air," in which one could well breathe, could also be obtained from minium.

A few weeks later he accompanied the Earl of Shelburne to Paris and could discuss his experiments with Lavoisier and other Paris scientists at Lavoisier's hospitable table. His host's attention was deeply roused for he had long busied himself with the problem of breathing and combustion without being able to solve it, although he had the best laboratory equipment at his disposal. When Lavoisier later on gave an impression that he had discovered oxygen himself, Priestley, by then in America, defended himself against this impudent claim by giving a detailed account of what had happened in Paris. For all that, Priestley remained loyal to the old phlogiston theory. Even his justification against Lavoisier was contained in a work that he wrote at a time (1800) when practically all other chemists had accepted the new oxygen theory and entitled "The doctrine of phlogiston established!"

According to Priestley, the "dephlogisticised air" discovered by him consisted of a mixture of nitric acid, earth and phlogiston; it was only later that he considered it a unitary element. Such weird views do not, of course, affect the value of his experimental findings. His experiments enriched chemistry with the following gases, hitherto unknown: "salt acid air" (hydrogen chloride) and the alkaline gas ammonia which is so eagerly absorbed by water that it could not be obtained earlier as a free gas. By working with mercury as sealing liquid he was able to obtain sulfurous acid or sulfur dioxide in gas form, also silicofluoride which decomposes in water. Finally, already in America, he discovered the poisonous carbon monoxide. Chemistry received these rich gifts

from the subsidiary occupations of a stubborn oddball.

Among the countries where chemistry flourished at that time was Sweden, which became absolute leader at the beginning of the 19th century through the work of Berzelius (1779-1848). Torbern Bergman (1735-1784), a specialist in analytical chemistry, held the chemistry chair at the old university of Upsala. He was the first to try to develop a systematic course of analysis for investigations in aqueous solutions. He used the blowpipe introduced in mineral analysis in 1746 by the Swedish mining councilor Sven Rinman (1720-1792), whose name still lives in "Rinman's green," used to trace zinc. Bergman melted various salts (soda, borax, microcosmic salt) over wood charcoal and pointed out the different effects of the inner and outer blowpipe flames. He was aided in these experiments by his pupil Johann Gottlieb Gahn (1745-1818) who developed blowpipe analysis into a separate method and passed it on to Berzelius.

Bergman also showed how cast iron, wrought iron and steel can be distinguished by their chemical behavior and cleared up the chemical composition of white lead—not an acetic acid compound as had been believed but a salt of carbon dioxide. He proved the acid nature of carbon dioxide and worked with other gases. A loyal adherent of the phlogiston theory, he was concerned with the problem of chemical affinity and further completed Geoffroy's "Table des rapports." He conceived affinity as an "attraction" of the smallest particles, corresponding to "gravity" (?). He coined the term "elective affinity" that Goethe used as the title of his novel. He tried to put some order into chemical symbols, still confused by alchemistic survivals, by introducing "generic symbols:" triangles for fire, air, water and earth; circles for salts and alkalis; crosses for acids; crowns for metals, etc. Bergman was considered the most important chemist of his time next to Markgrafe. But he refused membership in the Berlin Academy

on grounds of health. His glory gradually paled before the rising star of a much greater scientist.

This was Carl Wilhelm Scheele (1742-1786), perhaps the greatest chemist of all times. Scheele was a German who, because of the existing political conditions, lived in Sweden from his youth and is therefore considered a Swede by the Swedes.

The Scheele family has been traced for centuries in various North German cities: many documents name them as merchants, clergymen, teachers and high officials. A Scheele was bishop of Lubeck in the 15th century; after the 30 Years' War which gave Western Pomerania to the Swedes (1648) several Scheeles distinguished themselves in Sweden. One branch of the family was ennobled in Sweden. The territory did not return to Germany until 1815, a century and a half later. And so our Scheele was born under Swedish rule in the West Pomeranian capital of Stralsund on December 21, 1742. His father was a respected citizen and merchant, his mother's maiden name was Warnekros. The Scheele residence in the Faehrstrasse, coming from the mother's family, had to be given up in 1745 because of the bankruptcy of the father's business. (A Scheele museum was installed in it recently.) Little Carl Wilhelm grew up in rather straitened circumstances. He was educated in a private school managed by the Ph.D. candidate Smith, later frequented among others by the Greifswald chemistry professor Christian Ehrenfried Weigel (1748-1831), the real inventor of the Liebig condenser. Young Scheele took little part in his schoolmates' games; he tended to brood by himself and to busy himself with handicrafts like carpenting, turning or painting and showed an outspoken interest in the natural sciences. He tried to learn to read medical prescriptions and chemical symbols from a physician and a pharmacist. Already at 11 he is supposed to have expressed the wish to become a pharmacist because that pro-

fession offered him the sole possibility to fulfill his eager wish for an experimental study of nature.

And so he left school and parental home before he was 15 to become an apprentice of the Gothenburg pharmacist Bauch who came from Mecklenburg in North Germany. His eldest brother had also been an apprentice at this pharmacy of the Swedish city but had died at 20. Three other brothers became merchants; the youngest, Paul Joachim (1794-1825), studied medicine and died as city medical officer of Koeslin. At the "Unicorn" pharmacy at Gothenburg young Scheele could indulge in his thirst for science, fostered by his understanding master. He studied the partly obsolete textbooks by Kunkel, Neumann, Lemery and Boerhaave so intensively that Bauch wrote worriedly to his parents that the boy was reading day and night to the prejudice of his health. He also partly performed his experiments at night. A practical joke by somebody who did not like him involved him in an explosion that shook the house but did not quite have the serious consequences as the explosion that occurred 60 years later to Liebig and put an end to his pharmaceutical career. Scheele experimented with the all too few chemicals that existed in the pharmacy side by side with all kinds of drugs, herbs, roots, etc., and he gained a new observation from almost every substance he used. Like Liebig, he had an excellent memory so that every observation was retained in his mind. Scheele remained in Gothenburg after the end of his apprenticeship; he stayed there till 1765, when Bauch sold his pharmacy.

Scheele next worked for two years at Malmoe in the highly respected "Spotted Eagle" pharmacy of P. M. Kjellstrom. Here, too, he could follow his scientific pursuits. He spent almost his entire wages on good books, which he obtained from nearby Copenhagen. He gained a valuable friendship with a contemporary, Anders Johann Retzius (1742-1821) who later exchanged the pharmaceutical profession for the

academic and became professor at Lund. Retzius had a valuable educational influence on Scheele: he made him keep a laboratory diary to put some order into his experiments, hitherto performed quite arbitrarily and unsystematically. Retzius said of his friend that "his genius lay entirely in the sphere of physical sciences: he had no sense for anything else." Scheele conscientiously kept up the diary; it was published in 1892 by N. A. T. Nordenskjöld (1832-1901). Scheele used to visit from Malmö his family at Stralsund; on one such occasion he was painted on an ivory medallion by Brueggemann. This, the only authentic likeness of Scheele (he was 24 at the time), had a curious history. It vanished completely for a time; in it was located by the Swedish Pharmaceutical Society, after two years' search, with a Berlin family related to the Scheeles.

Scheele had but limited facilities to pursue his researches in Stockholm, where he came in 1768 to become an apprentice at the "Raven" pharmacy. He worked as a dispenser and could perform his experiments only in a narrow window niche. But even there he managed to make a remarkable discovery: the varying strength of the action of different parts of the solar spectrum on silver chloride. When his friend Retzius came to Stockholm, Scheele let him participate in his experiments. They chose cream of tartar for their research and proved that it contained a hitherto unknown acid. Scheele wrote a report on these investigations to Bergman at Upsala with a request to publish it. But when he heard nothing from Bergman he wrote up another report and handed it to Retzius, who was connected with the Academy, asking him to publish it. This Retzius did but, strangely enough, only under his own name; Scheele, who had contributed the lion's share to the experiments, was not even mentioned in the first scientific publication of his work. When Scheele sent another paper to Bergman, it appears that Bergman did read it at a session of

the Academy but then laid it aside, so that Scheele had some more disappointments in his first gropings towards publicity.

In 1770 Scheele moved from Stockholm to Upsala where he worked at the "Upland Arms" pharmacy, whose owner Ch. L. Lokk was also a scientist. Here Scheele occupied the relatively more independent post of head of laboratory, and he had more time for his own researches. He tried at first to avoid Bergman, because of his unpleasant experiences with him, but came into close contact with him in a strange way.

Bergman returned to the pharmacy a sample of saltpeter which he rejected because it developed brown vapors after heating with acetic acid. This phenomenon, which puzzled both the experienced pharmacist Lokk and the learned professor Bergman, was no mystery to the lab technician Scheele: he had often watched the conversion of nitric acid into nitrous with heating and could explain it as a normal phenomenon. But it was only when it was made clear to him that Bergman's unpleasant treatment of him was due not to hostility or disrespect but only to forgetfulness and slovenliness that Scheele could be persuaded to visit Bergman. The two totally unlike men became the best of friends: they supplemented each other excellently. As Retzius put it: "It is hard to see who was teacher and who pupil: while Bergman obviously got most of his practical knowledge from Scheele it was thanks to Bergman that Scheele's knowledge became so much clearer in his later years."

Scheele's experiments gained him such a reputation that he was asked to demonstrate them to Prince Henry of Prussia, brother of Frederick the Great, when he visited Upsala University laboratory accompanied by the Swedish Duke of Södermanland. The experiments and Scheele's personality made such an impression on the two princes that they suggested that the young man should be supplied with his own laboratory. Scheele, however, was not interested because he always

managed to perform his experiments with the minimum of equipment.

But he received another sign of public recognition: in February 1775 he was elected member of the Swedish Academy of Sciences, an honor never before or since bestowed on a pharmaceutical apprentice of 32. Shortly afterwards Scheele had his first offer of an independent position: that of administrator of a pharmacy at Koeping on Lake Maelar, whose owner had died in April 1775. He moved to Koeping in the summer of 1775 and, after overcoming unexpected initial difficulties caused by a prosperous rival, was able to purchase the pharmacy in the following year. For all these experiences he managed then—what he should have managed long before—to put together his observations and discoveries in a large treatise which he handed over to a publisher. But even then misfortune dogged him. His “Chemical treatise on fire” in which he described, among others, his discovery of “fire air” made in 1771-2, remained unpublished for two years, till 1777. By then Priestley’s discovery of 1774 had long become known and Lavoisier had given his famous lecture to the Paris Academy on April 26, 1775 so that Scheele feared that he would be regarded as a plagiarist. This proved not to be the case: Lavoisier himself very highly praised the contents of his book.

The year 1777 was most eventful for Scheele and led him to the pinnacle of his glory. No less a man than Frederick the Great tried to win him for his Berlin Academy. But the King had meanwhile forgotten the name of the capable Swedish chemist and the enquiries of the Prussian envoy at Stockholm reached the pharmacist “Scheel” or “Schell” in his provincial nest only in a roundabout way through Bergman and an unimportant member of the Mining Council. Scheele refused because he wanted to pursue his experimental investigations undisturbed. He took instead at Stockholm the examination



required from holders of independent posts, which his examiners turned into an act of homage to a famous man. He also used this opportunity to make his inaugural speech at the Academy. The king was present, and Scheele was honored by being made one of the two leading candidates for the presidency. He lost out to his rival, though certainly not to his sorrow, and returned, refusing all tempting offers, to his small pharmacy at Kocping to lead a laborious life in the service of chemistry. He by no means neglected his pharmacy, which he served with only one assistant from time to time. For a long time he used a kind of shed for a laboratory; but in 1782 he acquired a pretentious house on the town green, where he installed a laboratory of several rooms. It was here that he received some foreign visitors like the Spanish brothers d'Elhujart, who managed to obtain metallic wolfram from the wolframic acid discovered by Scheele.

Scheele had lived since the age of 15 in pharmacies and laboratories, without giving himself much rest. He worked with most poisonous substances like arsenic hydride and prussic acid, whose toxic effects had still to be tested. But he did not die of such a poisoning, contrary to later rumors. Three decades later, the Munich chemistry professor A. T. Gehlen (1775-1815) died of an arsenic hydride poisoning in a demonstration experiment. But Scheele, whose shed laboratory offered but insufficient protection against the weather, fell victim to a rheumatic-gouty illness which gradually became more and more painful. To this were added inflammations of the respiratory organs, which made him bedridden in the spring of 1786. As he was aware of the seriousness of his state he married the widow of his predecessor. Pohl, to secure the pharmacy for her and her son. Two days later, on May 21, 1786, this great and noble man breathed his last. The widow gave him the most distinguished funeral the town had ever seen—and shortly afterwards married the new

administrator of the pharmacy. There are monuments to Scheele at Koeping and Stockholm and there exists a detailed biography by O. Zekert.

Scheele's scientific work embraced almost all then existing areas of chemistry. He wrote in the introduction to his "Chemical treatise on air and fire": "The object and chief purpose of chemistry is to break up substances skilfully into their components, to discover their properties and to put them together again in different ways." And he wrote in a letter: "Truth alone is what we want to know and what a joy it is to have explored it." It was in this spirit and in this way that he pursued his experiments with unflagging enthusiasm. His first scientific publication (1770) concerned, as we already noted, the discovery of a new acid in cream of tartar and indicated a general method to trace different organic acids in vegetable and mineral substances.

In addition to the old-established acetic acid, succinic acid and benzoic acid, obtained by sublimation from benzoin resin, were known. Also, various chemists had obtained from the distillation of ants another acid, investigated in detail by Markgrafe in 1749; he obtained various organic salts of that acid but was unable to characterize it as organic acid. As late as 1802 formic acid was described by A. F. Fourcroy (1755-1809) and L. N. Vauquelin (1763-1829) as a mixture of acetic and malic acids; only in 1812 Gehlen finally proved that it was an independent organic acid. At the time when Scheele started experimenting with cream of tartar it was customary to refer all acid properties of organic substances to a content of acetic acid. Markgrafe had investigated cream of tartar in 1763 and made the important discovery that the potassium contained in it was not, as was believed previously, only created in heating but was an original component as "vegetable alkali." But Markgrafe did not bother about its respective acid.

Scheele now showed that the acids contained in organic juices could be separated through conversion into calcium or lead salts and then freed from the salts by the application of sulfuric acid. In this way he discovered tartaric acid in 1769, citric acid in 1784, malic acid in 1785 and gallic acid in 1786. In 1776 he obtained a peculiar acid by treating sugar with nitric acid. Bergman described it, after investigation, in his "Dissertatio de acido saccharico," without mentioning Scheele's name. But Scheele proved in 1784 that the "saccharic acid" that he had obtained was nothing but the "oxalic acid" found by J. Chr. Wiegand (1732-1800) in wood sorrel. Scheele discovered uric acid in 1776 when investigating bladder stones and lactic acid in 1780 when investigating milk. By treating sugar of milk with nitric acid, Scheele obtained yet another acid which he called "acidum sacchari lactis" or "acidum galactosaccharinum" which, he later obtained in a similar fashion from gum tragacanth. Fourcroy named this acid, which can also be obtained from the mucus of the plants, "mucic acid."

By treating olive oil with litharge Scheele obtained a peculiar oily fluid which he called, because of its sweet taste, "oil sweet," i.e., glycerine (1783). He obtained it also from other fats, without, however, explaining the actual saponification process. This was reserved to Michel Eugene Chevreul (1786-1889), the Frenchman who lived to be the Methuselah of chemists, in 1823. Scheele could convert his "oil sweet" into oxalic acid by the application of nitric acid and thus prove its relationship with sugar. He closely investigated prussic blue in 1782 and obtained, by the application of diluted sulfuric acid, its volatile and inflammable "coloring principle" which he called "Berlin blue (hydrocyanic) acid." From the mode of formation of potassium ferrocyanide Scheele concluded that this very volatile acid, whose name was later abbreviated to "blue acid," was composed of sal

volatile ( $\text{NH}_3$ ), atmospheric acid ( $\text{CO}_2$ ) and phlogiston (H). He also succeeded in using graphite instead of animal charcoal in obtaining cyanic compounds so that, if cyanides are considered compounds, Scheele should have the glory of being the first man to make an organic synthesis from inorganic substances, half a century before Woehler (1828). Another nitrogen compound of a peculiar kind was known to the alchemists as "fulminating gold." Scheele proved the gases escaping in the explosion were composed of nitrogen and ammonia.

In addition to some smaller investigation, of borax (1768) and "ice oil" ( $\text{SO}_3$ , the "philosophic salt" of Basilus Valentinus), whose real nature he recognized, Scheele made a detailed study of "stinking sulfuric air" (hydrogen sulfide) in 1776. He learned its development by the action of diluted sulfuric acid on various sulfur compounds—iron sulfide is most appropriate—and obtained it by heating sulfur in hydrogen gas. While Rouelle still believed that the sulfuric content of the gas was merely an impurity, Scheele proved that sulfur was the characteristic component of the "stinking air;" he also managed to obtain hydrogen persulfide as an oily liquid from alkalipolysulfides.

Scheele demonstrated that metallic iron, copper and mercury could appear in two "phlogisticised states" or, as we would put it today, in two degrees of oxidation. He studied in 1778-9 the two minerals molybdenite and graphite, which were often considered identical, and obtained from the former, (molybdena), through treatment with sulfuric acid, a white earthy mass which he called "molybdic acid" because of its acid property. Metallic molybdenum was obtained a few years later (1782) by the Swedish chemist Peter Jacob Hjelm (1746-1813). By treating graphite or "plumbago" with nitric acid Scheele converted it almost entirely into "fixed air," from which he concluded that graphite was

nothing but coal mixed with a little fixed air and phlogiston. He also proved that cast iron contained carbon (1781). When investigating scheelite he proved that it contained the calcium salt of a hitherto unknown acid. When the two Spanish chemists, Juan Jose and Fausto d'Elhujart, who studied at Upsala under Bergman, found the same acid in the wolfram mineral, but bound to iron and manganese, the new metal, which they managed to reduce, was named wolfram (1783). The mineralogist A. G. Werner (1750-1817) suggested that the metal be called "Scheel"; the name did not take, but "scheelite" did.

In 1771-1781 Scheele repeated Markgrafe's investigations of fluorspar, published in 1768. He proved that the volatile acid developed from it by the action of sulfuric acid did not contain silica. The silicic acid separated in water came from the glass vessel in which the mixture of fluorspar and sulfuric acid was heated; if lead vessels were used, pure hydrofluoric acid was obtained. He had to defend this view in the last year of his life against Achard who, in spite of everything, clung to his teacher's mistaken view. Like Cavendish, who did not publish his results, Scheele proved that arsenic could be further "dephlogisticised"; it could be converted, by aqua regia or chlorine, into an acid (arsenic acid) whose properties Scheele investigated. Thus he discovered in 1775 arsenic hydride, though he did not test its extraordinary toxicity. He also obtained the copper salt of arsenous acid. This was the "Scheele green" which, like the "Schweinfurt green" produced by Sattler in 1814 (arsenate and acetate of copper), was long popular for painting pictures and wallpapers, until its use was forbidden because of its great toxicity.

Bergman made Scheele perform in 1774 a thorough investigation of pyrolusite, whose chemical nature was still unknown and which was often confused with magnetite. The results were very fruitful indeed. By the action of hydrochloric

ric acid Scheele obtained a greenish gas, the "dephlogisticised hydrochloric acid," which was recognized to be an element only a generation later, in 1810, by Humphry Davy (1778-1829) and called chlorine. Scheele also proved that the main component of pyrolusite was an unknown "earth" which showed many similarities to lime. Scheele's friend J. G. Gahn (1745-1818) produced from it metallic manganese in 1780. Scheele also thoroughly studied the barite pieces sprinkled in the pyrolusite; he isolated them by melting with coal and alkali. He proved that they also contained an unknown "earth" which formed with sulfuric acid a salt soluble with particular difficulty. With these barium salts Scheele enriched chemistry with the most valuable reagent to sulfuric acid.

In the introduction to his most important publication, the "Chemical treatise on air and fire" of 1777, Scheele reports on his experiments to solve the question, propounded by the alchemists, of whether water could be turned to earth by persistent boiling. He kept a quantity of distilled snow water equal to half the old measure called "lot" boiling for 12 days and nights in an egg-shaped alembic with a narrow neck an ell long. The water gradually became milky and precipitated in cooling a white powder which proved to be "silica with a bit of lime," while a jelly-like silicious acid could be precipitated from water by acid. It was obvious from the state of the inner surface of the alembic that these precipitations came from the glass. The chief part of the "Chemical Treatise" is devoted to the problem of composition of air. To prove that air is composed of "elastic fluids of two different kinds" Scheele quotes not an experiment or two but goes to the trouble of mentioning no less than nine different chemicals that absorb part of enclosed air acting upon them for some time. Unlike Cavendish he thought little of quantitative determinations. Like Priestley he felt it was enough to state that

anything from a fifth to a third of air disappeared in the action of the various reagents, similarly as in the combustion of various substances, when he, e.g., took away the developing "air acid" with lime water. But he is not satisfied to decompose air into its components: he wants to put them together again artificially by mixing the "spoiled air" (nitrogen) with the fire-sustaining "fire air." But how? The experience he gathered in ceaseless experimenting came to his aid. He mentions ten different procedures to obtain "fire air," including the heating of saltpeter and mercury oxide, the usual methods. Scheele's methods included the heating of a mixture of pyroxilite and oil of vitriol, so that he called the resulting gas "vitriol air." By mixing it with a threefold quantity of "spoiled air" he again obtained atmospheric air. Unlike Cavendish and Priestley, he did use the "pneumatic bath:" "My apparatus," he wrote, "is of the simplest: I use alembics, retorts, bottles, glasses and ox bladders." Scheele's laboratory book proves that he performed these experiments, published in 1777, as early as 1771-2: he must be therefore granted priority in the discovery of oxygen. He supplemented his chemical experiments with "fire air" by respiratory experiments with different animals (rats, flies, bees) and himself. He proved by special experiments that "fire air" is converted into "atmospheric acid" in respiration as in combustion.

While Scheele proved here as elsewhere to be a brilliant experimenter, he was a total failure as a theoretical interpreter of the phenomena he observed. Like other chemists of his time he was an ardent adherent of the phlogiston theory. For him, too, phlogiston was "a true element and a quite simple principle" which cannot be obtained by itself. He tried to prove that fire heat and air consisted of "fire air" and phlogiston. Scheele did not live to witness the triumph of Lavoisier's new oxygen theory. But there is serious doubt

whether he would have, in that case, remained as faithful to phlogiston as Priestley.

Of Scheele's other work one might mention his experiments with phosphorus for which he created an improved method of manufacture from bones. He derived the brittleness of cast iron from its phosphorus content. He also demonstrated how vinegar could be kept for a long time by a kind of pasteurization and recognized that wood charcoal could absorb gases—a discovery that had many practical applications later, e.g., with gas masks.

In addition to the "Chemical Treatise" Scheele published in the Transactions of the Swedish Academy of Sciences (1770 through 1787) and in Crell's "Chemical Annals" (1784 through 1787). Scheele's collected works were published in Latin in 1788 by F. Hermbstaedt (1760-1833). They appeared in German in 1792 "Scheele's complete physical and chemical works." French and English translations were made from the German edition. His letters and notes were published in German in 1892 by A. E. Nordenskjöld.

#### 4. *Resume of Phlogiston Era*

To get a proper understanding of the different stages in the historical development of chemistry it is not enough to judge them from the point of view of chemistry today. One must also understand how they grew out of the conditions of the time and appreciate them as stepping stones to higher stages. Such considerations are particularly important with the phlogiston theory which is often dismissed as a piece of incomprehensible lunacy. But if only because this peculiar theory was the ruling idea for some 100 years and some first rate natural scientists adhered to it, it is worth while to give more thought to estimating its value and importance.

The real value of a scientific theory lies in the possibilities



it creates to order the manifold observations obtained according to definite points of view and to bring them into a meaningful relationship. It is only of secondary importance whether the theory is "right" or "wrong": the further development of science decides this point. The phlogiston theory founded by Becher and further developed by Stahl brought for first time, after overcoming alchemistic and iatrochemistic views, a meaningful order into most varied chemical phenomena like combustion, calcination of metals, respiration, fermentation, etc. It did it by assuming in all these cases as a uniformly effective principle a hypothetical "something" which, appearing visible in the flame, was called "phlogiston." It had been observed for long that metals actually gain weight in calcination in spite of the escape of phlogiston. But that was no sufficient counterproof against the correctness of the phlogiston theory since the concepts of weight and gravity remained quite unclear. The famous professor J. R. Spielmann (1742-1783), under whom Goethe studied chemistry and botany, said in his "Chemical institutions" of 1763 that he did not dare to offer a reason why the weight of lead increased in calcination because the cause of gravity was unknown. The prevailing view was still qualitative and it was hoped to find later some kind of explanation for this mysterious phenomenon.

But some thinking scientists tried to solve the question experimentally, and in two main ways. One was to assume (confusing absolute and specific gravity) that the metal and phlogiston had different gravities. The lighter phlogiston diminished the weight of the metal, just as a cork of the fishing line makes its lead swim in water. This view was represented by the French chemist Chardenon in a treatise published in the "Memoires" of the Dijon Academy in 1769 and also by Guyton de Morveau (1737-1816). Or else a negative weight, an "absolute levity" was ascribed to phlogiston. Such a theory

was developed by the Halle professor F. A. Gren (1760-1798) in his "Inaugural dissertation on the genesis of fixed and phlogisticised air" of 1786. This recalls the Aristotelian elements of which earth was the downward tending heavy principle and fire the upward tending light principle, while water and air moved at a medium height.

The views of the phlogiston chemists become more comprehensible when viewed from the point of view not of material processes but of energetics. In combustion, not only a flame escapes but heat is developed. This fact, directly perceived by the senses, is not taken into account in a purely material interpretation of the process. But if we replace "phlogiston" by "energy" one can do some justice to the physical and chemical phenomena in the absorption of oxygen. The phlogiston chemists, for all their confused concepts, had some inkling of this, and so they felt they had solid ground underfoot. And so it becomes comprehensible how such views could be held and defended by men of considerable intellectual stature. The last epigones of the phlogiston theory, Baron L. Von Crell (1744-1816), founder of the "Chemical Annals," and Scheele's Swedish friend A. J. Retzius (1742-1821) remained faithful to it till their death. After they died, Lavoisier's oxidation theory triumphed everywhere.

### *5. Brief Survey of the Prehistory and History of the Discovery of Oxygen*

The discovery of oxygen has a long prehistory that shall be briefly summarized here. The Italian genius Leonardo da Vinci (1452-1519), equally great as artist, engineer and scientist, had already expressed the view that air was not one element, as was believed till then, but consisted of two components, of which one was consumed in combustion and respiration. But this insight remained unnoticed. It was be-

lieved, on the contrary, that both in combustion and in the calcination of metals a certain volatile substance was given up to the air but the process remained unexplained. The French physician Jean Rey (died 1645), asked by the pharmacist Brun to explain why metallic tin and lead gained considerable weight in calcination through prolonged heating in air, published in 1630 some papers entitled "Essays on finding out why the weight of tin and lead increases in calcination." Rey argues that air possesses like all natural substances a certain gravity and therefore produces increased weight in calcinated metals, just as sand becomes heavier when wet with water. But he did not explain the real nature of calcination. This question, together with those of combustion and respiration, became more and more prominent.

Ralph Bathurst (1620-1704) was a theologian forced by political troubles under Cromwell to exchange his parish for a medical career and later returned to his original profession. In 1654 he became a doctor of the Oxford medical faculty with his "Three essays on respiration," where he develops the following view. In respiration a certain nutritive substance—he calls it "nitrous food"—is absorbed. It is also present in saltpeter, which is so helpful to plant growth as artificial fertilizer, as well as in rain water. It also acts as bleaching agent on clothes. This nitrous matter is absorbed in respiration by blood and distributed in lungs and veins to other bodily organs, where it is as nutritious as solid foods. Respiration, like combustion, cannot take place if air is excluded.

Robert Hooke (1635-1703), also assumed a nitrous component of air in his "Micrographia" of 1665, which primarily deals with the coloration of thin leaves. His explanation of combustion is that a certain component of air has the capacity to dissolve all combustible substances under high temperature. This component is contained in large quantities in salt-

peter and this was why the latter so favored combustion.

John Mayow (1645-1679), who unfortunately died young, came much more closely to the real solution. In his Oxford dissertation of 1669 "Two treatises on respiration and rickets" which he expanded into the "Five physico-medical treatises" of 1672. He calls the air component which maintains combustion and respiration the "nitro-aerous," "fiery" or "vital" spirit. He views it as an element in gaseous state, which is contained in saltpeter and which, e.g., makes it possible for a mixture of sulfur and saltpeter to burn under water. With the aid of nitric oxide, which he obtained from nitric acid and iron, Mayow even tried a quantitative determination of this effective component in air but he was unable to get hold of it. Two generations later, Boerhaave, still busy with the same task, exclaimed "Happy is he who will discover it!" Mayow who was on the right path with his experiments (including some on animals) remained practically unnoticed.

By a curious coincidence, Becher's "Subterranean physics" appeared in the same year at Munich as Mayow's "Two treatises" at Oxford. These two writings are like signposts on an important crossroads of chemistry. The latter did not follow Mayow but Becher and reached the final discovery of oxygen only over the detour of phlogiston.

The first man to develop oxygen in a free state, without however correctly recognizing it as such, was the Danish polygrapher Ole Borch (1620-1690). In his 1674 treatise "Nitrum non inflammarī" he reports that coal burns fiercely on saltpeter because the effective component compressed in it is blown out of it, as if with bellows. He could obtain this gas by simple heating of saltpeter but could not receive it separately from the air because the pneumatic bath was not invented by Stephen Hales until half a century later (1727). Hales himself obtained oxygen, mixed with carbon dioxide, by heating saltpeter with pulverized animal charcoal. But,

although he knew Mayow's treatises, he did not investigate this gas more closely, any more than other gases he developed. All that interested him was the quantity of the gas developed.

One might mention in this connection the Russian genius V. Lomonosov (1711-1765). He was a man of very many talents—he was one of Russia's first lyric poets—who started life as a simple peasant and died Academician for chemistry and mineralogy of Saint Petersburg. He was educated mostly in Germany, at Marburg University and the Freiberg Mining Academy. He freed himself from phlogistic views and recognized that a part of air was consumed in combustion; but he gave no fuller explanation of the process.

The true discoverer of oxygen was Carl Wilhelm Scheele, who made his experiments in 1771-72. But as he did not publish until 1777, Priestley came before him with his discovery of August 1, 1774 and Scheele's merits were not recognized until much later. But Pierre Bayen (1725-1787), inspector of French field pharmacies in the Seven Years War, obtained even before Priestley—in Spring 1774—also by heating red mercury oxide, an "elastic fluid" in which mercury was again converted in heating into "mercurius precipitatus per se." These experiments proved that a calcinated metal could be converted into metal without addition of phlogiston, indeed with delivery of a gas. Bayen himself could not understand the results of his experiments, which he published in April 1774. He had, so to say, the key to the great mystery in his hand but did not know how to use it. If he had only held a small burning taper in his "elastic fluid," he would have discovered oxygen instead of Priestley, with all the attendant glory. But since he overlooked this small but decisive experiment, he lost the glory.

Lavoisier developed his oxidation theory on the basis of Scheele's and Priestley's experiments and thus properly completed the discovery of oxygen. We can speak of a "synthesis

of discovery" here. It was not the discovery of a hitherto unknown element. By finally explaining the oxidation processes and simultaneously determining the decisive importance of weight ratios in all chemical processes, Lavoisier started a new era in chemistry. Hitherto the essential preoccupation with substances had been qualitative. But now a quantitative method was developed, in which concepts of measure, number and weight played the leading part. After Jeremiah Benjamin Richter founded stoichiometry in 1792 and John Dalton revived the classical atomic theory in 1803, chemistry, often linked with physics in various ways, could reach its present high level of theoretical and practical achievement as a science.



## PART TWO

### FROM THE DISCOVERY OF OXYGEN TO THE PRESENT

The discovery of oxygen started a new epoch in chemistry. The two discoverers, Scheele and Priestley, dug the grave of the all-dominant phlogiston theory. They did not realize what they were doing—they remained faithful believers in the phlogiston theory till their respective deaths. A correct theoretical interpretation was still required to evaluate the experimental results and to find a way out from the ever more confusing jungle of phlogistics. The hitherto practiced qualitative investigation had to be supplemented by strict quantitative methods, unconditionally founded upon measure, weight and number. Only this could sweep away obsolete views and produce the great transformation of chemistry.



## V. DEVELOPMENT OF CHEMISTRY FROM THE DISCOVERY OF OXYGEN TO THE MID-19th CENTURY

### 1. *Transformation of chemistry by Lavoisier's oxidation theory.*

The great transformation, that was finally accomplished only by the discovery of oxygen, was not started by a chemist. As had so often happened before, the great reformer came from a neighboring area of science. Lavoisier was a physicist. He barely made any significant chemical discovery; but he knew how to interpret experimental results with a clear and sober reasoning and thus make them serviceable to science in their true significance.

Antoine Laurent Lavoisier (1743-1794) was the son of a prosperous Paris lawyer who was raised to hereditary nobility as royal "secretary-counselor." The son did not follow in his father's footsteps but instead studied the natural sciences, especially physics. He also attended the chemical lectures of the famous Rouelle. He soon showed evidence of great talent. At 21 he gained a royal gold medal in a competition organized by the Academy of Sciences for the best method of lighting the streets of large cities. He made a geological trip that led him to Switzerland and joined the Academy at 25 as "supernumerary chemical adjunct." A few years later he became one of the "general farmers" to whom the collection of royal taxes was farmed out. He married the 14-year-old Pierrette Paulze, daughter of a very rich "general farmer."

The marriage was childless but Pierrette proved a valuable assistant in Lavoisier's scientific work in addition to organizing a lively social life in their family mansion. Lavoisier's great variety of talents and extraordinary zeal for work caused him to be consulted as an expert in all kinds of questions: food control, water supply on seagoing vessels, mesmerism, divining rods, balloon travel, etc. He managed to keep going in spite of all these demands by keeping a strict schedule, with the early morning and late evening hours devoted to science. To all this was added in 1776 the management of powder manufacture. He set up a laboratory at the "Salpetriere" hospital, fitted with the best and most sensitive physical apparatus, and employed competent assistants. With his liking for the dramatic Lavoisier organized there a weekly demonstration session, to which the most distinguished scientists of Paris were invited.

By acquiring a farm, Frechines, Lavoisier came into contact with politics as well as agriculture. He was elected to the provincial administration of Orleans and after the revolution of 1789 became a member of the Paris city council and an administrator of the royal treasury. He naturally took part in the elaboration of the new metric system of weights and measures. He was drawn into the ever more violent whirlpool of revolutionary politics and was arrested in November 1793 together with the other "farmers general." Only three of his many friends, including the mineralogist Haüy, dared to intervene in his favor. But the president of the tribunal made his famous reply: "We no longer need scientists." On May 8, 1794 he went to the guillotine with 28 other "farmers general" and, as the contemporary phrase went, "sneezed into the sack."

Lavoisier's scientific endeavors were really concerned with physics. Together with the mathematician Pierre Simon de Laplace (1749-1827) he constructed an ice calorimeter, with

which they obtained very exact determinations of specific heat and latent melting heat of various metals. They also made physiological experiments to determine heat developed by physical and mental work. Lavoisier tried to prove experimentally that weight remains constant in chemical processes and that matter is indestructible. The way in which he experimentally disproved the alchemist view on the conversion of water into earth is typical of the man. While Scheele offered a chemical proof, Lavoisier showed that the weight of the precipitation formed in the boiling of water was equal to the weight of the glass lost. He made no experimental discoveries in chemistry. His proof that gypsum was composed of lime, sulfuric acid and water was already given by Markgrafe in 1750.

Lavoisier's chief preoccupation for many years was the problem of combustion and calcination, respiration and fermentation, that so many scientists had tackled without decisive success. It was known for a long time that the weight of tin and lead increased in calcination. As early as 1630 Jean Rey tried to explain it in his "Essays." Lavoisier now showed that in the reduction of calcinated metals by heating with coal there develops an about thousandfold volume of "fixed air." In 1772 he repeated the experiment performed in 1694 in Florence by Giuseppe Averani (1662-1738, professor of jurisprudence at Pisa) and Cipriano Antonio Targioni (1672-1748, a Florentine physician). Lavoisier "evaporated" a diamond in the focus of a giant burning reflector, dating from Tschirnhaus' days. He obtained the same "fixed air" and concluded that diamond was nothing but pure carbon. Hanke-witz, the laboratory assistant of Boyle, and Markgrafe had already noted that the weight of phosphorus increased in combustion. Lavoisier noted the same phenomenon in the combustion of sulfur and tried to secure his priority for both these observations by depositing a sealed communication with

the Academy of Sciences in October 1772.

While Lavoisier was busy with such experiments and eager to solve the great riddle of the combustion and calcination processes he received in 1774 some unexpected help from Priestley. The latter came to Paris as Lord Shelburne's private secretary and was Lavoisier's guest along with other scientists. Priestley told the company of his experiments with the "dephlogisticised" air obtained from red mercury "precipitatus per se" and of its surprising property. His host and fellow guests listened to him astonished. This had to be the "fluide elastique" recently reported by Bayen without having tested its properties. Scheele, too, had written of a "vitriol air" or "fire air" he had obtained, besides "fixed air," by heating the precipitation of a silver solution to which soda had been added. Lavoisier immediately recognized the great importance of what he heard and read. As soon as his many occupations permitted him, he repeated the experiments with the rich means at his disposal and found their results correct. Next spring, on April 25, 1775, he lectured to the Academy on "the nature of the principle which unites with metals in their calcination and increases their weight." But he never mentioned Priestley, Scheele or Bayen. In the textbook he published 14 years later (1789) he writes in connection with oxygen that the gas had been discovered by Priestley and Scheele "almost at the same time" as by himself. This made Priestley, then in America, write his counterblast of 1800.

But it took several years even to a man thinking as clearly as Lavoisier to get rid completely of the traditional views. He held oxygen to be a compound of the actual "acidifying principle" or "oxygenating principle" with the "heat matter" still universally accepted in the physics of his time. The name "oxygen" is a simplification of the "oxygenating principle" (principe oxygene). (The German "Sauerstoff" means "acid matter.") It was recognized to be the element that not only

plays a decisive part in the formation of acids but also combines with metals to form "limes" or "oxides."

Lavoisier spent the then considerable sum of 50,000 livres on experiments to determine the chemical composition of water without achieving any substantial results. It was after the English physician and naturalist Charles Blagden (1748-1820) told him on a visit to Paris in 1783 of Cavendish's experiments that he and Laplace performed the experiments that proved that oxygen combined with hydrogen produced not as was expected, an acid but ordinary water. He again lectured on the matter to the Academy, without mentioning the name of the real discoverer. A sample of 45 grams of synthetic water is still preserved in Paris in a fused glass tube as a valuable Lavoisier relic. In later experiments Lavoisier succeeded in decomposing water by passing water vapor over incandescent iron powder; but he could recover only the hydrogen. •

By the 1780's Lavoisier's views of the chemical processes had cleared sufficiently for him to proclaim the phlogiston theory to be completely surpassed and to develop his own oxidation theory. Everything was turned upside down: separation (of phlogiston) became union (with oxygen) and union became separation. The new theory made slow headway, even among Lavoisier's inner circle. Berthollet (1748-1822) wrote within a phlogistonic system as late as 1785; Fourcroy (1755-1809) accepted Lavoisier's theory only in 1786-7 and Guyton de Morveau (1737-1816) did it still later. When the theory was called "the theory of French chemists" Lavoisier protested his exclusive rights, this time justifiably, saying "It is mine." Together with the three scientists named above Lavoisier worked out the necessary new nomenclature for chemical compounds and processes and published it in 1787 as "Method of chemical nomenclature." The names given there like oxyde de plomb, sulfate de baryte,

acide sulfurique, acide sulfureuse, etc., were duly translated into foreign languages and became part of their chemical nomenclature. Lavoisier's textbook "Elementary treatise of chemistry presented in a new order and according to recent discoveries" came out in 1789. Although light and heat still figure in it as weightless basic substances among the elements, the basic transformation of chemistry can be said to be completed by the appearance of this book. The chemical revolution was over just as the political started.

Lavoisier, with his incurable theatrical sense, celebrated this fact by a special performance. Phlogiston, prepared of inflammable material, appeared on the stage and was accused by Oxygen of heavy crimes. Stahl defended it acting as the "devil's advocate" but it was condemned to death by fire. The sentence was duly executed, with Madame Lavoisier acting the part of sacrificial priestess.

Lavoisier's papers mostly appeared in the "Memoires de l'Academie des Sciences" of 1768-87; some came out in the "Journal de Physique" and some in the "Annales de Chimie." The turbulent events of French foreign and domestic politics in the following decades delayed the publication of his collected works. The six heavy volumes of the "Works of Lavoisier," edited by Dumas and Grimaux, appeared only in 1862-1893.

The new oxygen theory gradually spread outside France. A German translation of Lavoisier's "Elementary treatise" by S. F. Hermbstaedt (1760-1833, court apothecary and professor of pharmacy in Berlin) appeared as early as 1792. Under the name of "antiphlogistics" the new theory fought the old. The Swiss physician Christoph Girtanner (1760-1800), who settled at Goettingen, fostered the spread of the new view in Germany. His books "New chemical nomenclature for the German language" (1791) and "Primer of antiphlogistic chemistry" (1792) contain, however, in addi-

tion to much that is good, innumerable errors. The last adherents of phlogiston died with Lorenz Friedrich von Grell (1744-1816, professor at Helmstedt and, after Helmstedt University was abolished in 1809, at Goettingen) and Scheele's old friend Anders Johann Retzius (1742-1821, professor at Stockholm).

## *2. Development of quantitative methods* (stoichiometry, revival of atomic theory, gas laws)

After Lavoisier (following the acceptance of his oxidation theory), made every one realize the importance of measure, weight and number, the next task was to investigate the weight ratios of the interreacting chemical substances and to clear them up on the theoretical level. The hitherto qualitative chemistry had to be supplemented by quantitative methods and concepts. The exact analytical balance became one of the most important tools of chemical investigation.

Lavoisier's collaborator Louis Bernard Guyton de Morveau (1737-1816, originally a lawyer, later professor of chemistry in Dijon and Paris) investigated in 1787 the quantitative relations in the conversion of two salts at the instigation of Richard Kirwan (1735-1812, also a lawyer, later natural scientist and president of the Royal Irish Academy in Dublin). He found that in the double conversion of the neutral salts potassium sulfate and sodium nitrate, two other neutral salts, sodium sulfate and potassium nitrate, are formed, without any uncombined residue of either base or acid. But since he did not follow up this important single observation with further investigations he could not derive from it a general law of neutrality. Christian Frederick Wenzel (1740-1793, first bookbinder, then surgeon, later chemist at the Meissen

porcelain works and director of the Freiberg foundries) occupied himself with similar problems in Germany a decade earlier. In his "Lectures on the chemical affinity of bodies" of 1777 he recognized the chemical mass effect by showing that the reaction speed in the action of acid on metal is in direct proportion to the strength of the acid. He also assumed a definite weight ratio of acid and base for the "middle salts" (neutral salts) but some inaccuracies in his most carefully conducted chemical determinations prevented him from really discovering the neutrality law. This discovery was reserved for a man who devoted his whole life, with admirable idealism, to the single task of introducing mathematics into chemistry: Jeremiah Benjamin Richter (1762-1807).

Born at Hirschberg in Silesia, Richter became a soldier at the early age of 16, against his wishes and inclinations, but under the influence of his uncle who was a military engineer and city architect of Breslau. After seven wasted years, the 23-year-old Richter was able to fulfil his dearest wish and to go to Koenigsberg University to study mathematics, natural science and philosophy. But Koenigsberg offered him nothing in chemistry, with which he had already busied himself both on the theoretical and the practical side. He was all the more influenced by the philosopher Kant (1724-1804) who said: "Natural science contains only as much science as it contains mathematics." After four years' study Richter got his doctorate in April 1789 with a dissertation on "The use of mathematics in chemistry." This thesis, which was like a program for the further development of chemistry, not only indicates the importance of mathematics for the clarification of chemical concepts and views but also points out the great practical usefulness of mathematical calculations for chemical engineering.

Bitter poverty forced Richter to give up in 1790 his academic teaching. For a few years he struggled as surveyor in



Silesia and later (1795) as assayer. In 1798 he was appointed "second arcanist" to the Royal Porcelain Works in Berlin. He was constantly busy with scientific, experimental and literary work, and had to earn the means required for his chemical investigations by such subsidiary occupations as the manufacture of exact areometers, working in the early morning and late evening. He spent his nights in translating French books and exhausted his strength prematurely. Like Scheele he sacrificed his life to his science and died in his prime at 45.

From 1791 through 1802 Richter published eleven volumes of his works under the title of "On the modern objects of chemistry" and with a motto "God ordered everything according to measure, number and weight" (Wisdom of Solomon, Chap. II, v, 22) which he put in the Greek language of the Septuagint. His chief work "Origins of stoichiometry or the art of measuring chemical elements" appeared in three volumes in 1792-3. He outlines there his new theory of the constant combining weights or "equivalent weights" of the chemical elements with the use of numerous examples. Richter is the discoverer of chemical equivalence and of the neutrality law. He also introduced the term "stoichiometry" (from the Greek "stoicheion," element). But although he saw things clearly, he was still adhering to the views of phlogistic chemistry which affected his powers of expression and made his writings difficult to read. Another difficulty was that Richter did not refer the values of the various equivalent weights to a common basis and to a real system. This was done for him by Ernst Gottfried Fischer (1754-1831, mathematics professor at the Coelln Gymnasium in Berlin). When translating Berthollet's "Researches on the laws of affinity" (1801), Fischer made a single table of Richter's equivalent weights by converting them with reference to sulfuric acid taken as 100. Berthollet incorporated the table of equivalent weights

into his "Essay on chemical statics" of 1803 and made it widely known.

With his mathematical outlook Richter also recognized certain regular ratios between the combining weights of the various elements. He ordered the alkaline and alkaline earth metals into an arithmetic series and thus made a first attempt at a periodic system of elements. But this attempt, successfully completed by two other scientists a couple of generations later, proved fatal to him through a stroke of malicious misfortune. He tried to fill a lacuna in his series with the "August earth," discovered by the Erfurt pharmacy professor Johann Bartholomaeus Tromsdorff (1770-1837). But this proved to be phosphate of lime and Richter's stroke of genius, represented by his attempted periodic system, fell victim to the ensuing ridicule.

Richter was not only great as a theoretician; he also has great achievements to his credit in analytical and preparative chemistry. He worked out in the Porcelain Works laboratory a separation process for cobalt and nickel and a new method to produce purple of Cassius. On this occasion he closely investigated the hitherto quite unknown properties of colloidal solutions.

A strange misfortune dogged Richter and his scientific work. Under the influence of his great teacher Kant he did not absorb the atomic idea, whose application would have made his new theory much more easily assimilable. It was only in the year he died that Dalton's atomic theory became accessible to the general public through T. Thomson. And when Richter's own laboriously gathered achievements were recognized, it was not he but Wenzel who was proclaimed to be the discoverer of the equivalence and neutrality law, owing to an error of Berzelius. It was only a generation later, at Saint Petersburg, that H. H. Hess cleared up the fatal mistake and Richter's achievement was duly recognized. Strangely enough,

Hess suffered a similar fate as founder of thermochemistry.

The important French chemist Claude Louis Berthollet (1748-1822) had views very different from Richter's. He was professor in Paris and Napoleon's scientific adviser in Egypt and Italy; he founded the "Societe d'Arcueil," with a scientific magazine, at his country home at Arcueil near Paris and worked with ammonia, hydrosulfuric acid, prussic acid, chlorine and its bleaching effect, etc. Berthollet held that the quantitative composition of chemical compounds was not constant but depended on the quantities interreacting in each case. This opinion was based on the correct idea of the mass effect law foreseen by Wenzel. His countryman Joseph Louis Proust (1755-1826; pharmacist in Paris, then professor at Segovia and Madrid, returned to France after losing all in the war, finally active at Angers), on the other hand, tried like Richter to prove the constancy of the composition of chemical compounds or the law of constant proportions through careful quantitative analyses. This involved him in a controversy with Berthollet that lasted many years.

The experimentally discovered laws became generally assimilable only by the introduction of a new conceptual framework. This was done by John Dalton's (1766-1844) quantitative atomic theory, which decisively affected the further progress of all physics and chemistry.

John Dalton was born in Eaglesfield in Cumberland, the son of a poor weaver. He received a good education in mathematics and the natural sciences, and his further education was fostered by a wealthy friend of his father, the instrument maker Robinson. Dalton had an early urge to transmit to others the knowledge he had acquired. A born teacher, he taught at 12. boys older than himself, and became at 15 teacher at a private school kept by a close relative in the neighboring Kendal. He continued his teach-

ing activities with great devotion throughout his life by teaching at schools or giving public lectures. From 1793 he was employed by the Warrington Academy at Manchester, where Priestley had previously taught. When the Academy was moved from Manchester in 1799, Dalton stayed in the city, continued his scientific activities and tutored. He became member of the Literary and Philosophical Society (and its president from 1817 onwards) and set up a laboratory in its building. While he was at first especially interested in meteorology and other sciences, his interest in chemistry was first roused at Manchester. His scientific achievement gradually received public recognition. The Royal Society made him a member in 1822 and bestowed on him its gold medal in 1826. He became an honorary doctor of Oxford and Edinburgh Universities and received a small royal pension from 1833. He discovered in himself the red-green color blindness still called in English "Dalton's disease" or "Daltonism." Even at the height of his fame he remained a simple and modest man.

Dalton's scientific work started from meteorology and led him by investigations of the atmosphere to chemistry and gases in general. Since he investigated all processes with exact measurements, he discovered about the same time as Gay-Lussac, the law of the constant heat expansion of gases. Strangely enough he found the same value ( $0.00375=1/266$ ) for the heat expansion coefficient as Gay-Lussac. It was only much later that this value was independently corrected by two other scientists, the German physicist Gustav Magnus (1802-1870, professor in Berlin) and the Frenchman Henri Victor Regnault to ( $0.00365=1/273$ ). In correct air analyses with nitric oxide Dalton discovered that the oxygen content of air remains constant and independent of height. He found that each gas in a mixture of gases behaved as if it were alone in the space and that the total pressure of the mixture

was equal to the sum of individual pressures. He could thus confirm the law discovered by his friend, the manufacturer William Henry (1774-1836), in 1803 that the solubility of gases in different liquids corresponded to the pressure exercised in each case.

On October 21, 1803, Dalton lectured to the Manchester Literary and Philosophical Society on the results of his absorption experiments. He used this opportunity to make the laws he discovered clearer by adding some general theoretical considerations on the nature of gas particles. It was in these additional thoughts, which he expounded to a total of 7 listeners, that Dalton gave a brief account of his atomic theory and read out the values he obtained of the "relative weight of the smallest particles" of six elements (H, N, C, O, P, S) and 13 chemical compounds.

This first table of atomic weights, which were still very inexact, was published in 1805 in the Transactions of the Society. It attracted no notice, however, until Thomas Thomson (1773-1852, a physician who rendered great services to chemistry by his many investigations of plants and minerals and some excellent textbooks) became an ardent Daltonian and published the table in a third edition of his book "A new system of chemistry" (1807). Dalton's own chief work, "A new system of chemical philosophy," in which he expounded his atomic theory in the chapters on the constitution of bodies and on chemical composition and included an improved and extended table of atomic weights, started publication only in 1808.

Dalton imagined the atoms to have spherical form and represented them as small circles, with different elements symbolized as additional dots and lines. The previous chemical symbols, dating from the alchemistic era, had only qualitative significance. This still applied to the symbols for elements—lines, triangles, squares, semicircles—pro-

posed in 1787 under the influence of Lavoisier by Jean Henri Hassenfratz (1755-1827, French mining and foundry specialist who collaborated for a time with Lavoisier) and Pierre Auguste Adet (1763-1832, professor in Paris). But Dalton tried to introduce a language of quantitative symbols in which each symbol stood not only for a definite element but also for an atom of a definite weight. He also composed molecular formulas, in which he assumed the simplest composition. Thus water was composed of one atom of hydrogen and one of oxygen  $\odot \bigcirc$ , ammonia of one of nitrogen and one of hydrogen  $\ominus \odot$  and so on.

When Dalton's symbols became insufficient for the increased number of elements, other people put the initial letters of the elements' names into his circles instead of the dots and lines. Dalton rejected this innovation as he rejected almost any innovation not originated by himself.

In 1804 Dalton developed from his atomic theory the law of multiple proportions which he proved correct by a quantitative analysis of methane ( $\text{CH}_4$ ) and ethylene ( $\text{C}_2\text{H}_4$ ). But generally he was so convinced that his atomic theory was correct that he held it unnecessary to provide experimental proof. This was done by other scientists.

Among them was William Hyde Wollaston (1766-1828). He was originally a physician but soon devoted himself entirely to physical and chemical investigations. In 1804 he discovered the metals palladium and rhodium, and also discovered a method to make platinum forgeable. In 1809 he proved that the newly discovered elements titanium and columbium were identical. Wollaston confirmed the law of multiple proportions by proving that the carbon dioxide content of neutral and acid carbonates was as 1:2. He also introduced the term "equivalent," but since he also used it in the sense of "atom" he started a confusion of concept which took long scientific debates to clear up. He also dealt

with the arrangement of atoms in space and indicated the tetrahedral pattern some 65 years before Le Bel and van't Hoff. A number of other scientists, headed by Berzelius, set themselves the task of exact determination of atomic weights.

The most important French physicist and chemist of the first part of the 19th century was Joseph Gay-Lussac (1787-1850).

Born the son of a lawyer at Saint Leonard in Limousin province, Gay-Lussac received a Paris education, in which he was favored by Berthollet. No difficulty or danger could stem his scientific zeal: twice he suffered heavy injury during his experiments. To investigate the atmosphere he went up several times in a balloon to a height of some 23,000 feet. It was at Berthollet's house at Arcueil that he met Alexander von Humboldt who had just returned from his great journey. Together they made experiments to determine the inter-reacting quantities of gases, travelled to Italy and spent the next winter in Berlin. Later Gay-Lussac became professor of physics and chemistry at various Paris scientific institutions—the Sorbonne, the Ecole Polytechnique, the Botanical Gardens, the University. From 1809 through 1849 he edited the "Annales de Physique et Chimie" together with Dominique Francois Arago (1786-1853), professor at the Ecole Polytechnique.

Gay-Lussac's scientific achievements are manifold. In 1802 he discovered, simultaneously with Dalton, the law of the uniform heat expansion of gases. In 1805 he proved with Alexander von Humboldt that the volumes of the inter-reacting quantities of the gases oxygen and hydrogen, incorrectly calculated by others, were exactly as 1:2. He completed this observation in 1808-9 by experiments with other gases ( $\text{NH}_3 + \text{HCl}$ ,  $2 \text{SO}_2 + \text{O}_2$ , etc.), into a general rule that the volumes of inter-reacting gases and of the resulting gaseous compound are in simple proportion of integral num-

bers. He also contributed to chemistry by other important work. After Courtois' discovery of iodine, he carefully studied the properties of the new element and produced hydrogen iodide, iodide salts and free iodic acid. He also produced liquid hydrocyanic acid in 1815 and determined its composition. It was shown in this connection that cyanogen (CN) can also exist in a free state as a composite radical; Gay-Lussac thus gave the first example for the theory of radicals that was to become so important later on. He prepared the way for the concept of isomerism by showing through correct elementary analysis that various organic matters with quite different properties (cellulose, sugar, starch, gum) had the same percentual composition. He obtained oxalic acid by heating wood shavings, cotton, sugar, etc. with caustic potash. He used a correct determination of the boiling point of organic liquids to test their purity. He made detailed experiments with many sulfur compounds. He invented the Gay-Lussac tower for the absorption of nitrous gases in 1827, which considerably improved the manufacture of sulfuric acid. He is also the real founder of volumetric analysis or titrimetry, which proved greatly useful both to theoretical and industrial chemistry. He coined the terms "burette" and "pipette." He introduced chlorimetry (determination of chloride of lime) in 1824, alkalimetry (determination of soda) in 1828 and the determination of silver and chlorides in 1832.

Gay-Lussac's most important scientific collaborator was Louis Jacques Thenard (1777-1857, there is no accent on the "e" of his surname, though it is often put there). He was of peasant origin, studied under Vauquelin and Berthollet, became chemistry professor in Paris and was later raised to the nobility and became peer of France. Together with Gay-Lussac he obtained free boron and fluoric acid almost free of water. After Davy discovered the alkaline and earth alkaline metals they showed that these could be obtained not



only through the electric current but also through heating the oxides with iron or coal. They also obtained in 1810 the amines and superoxides of potassium and sodium and converted barium oxide into a superoxide by heating in air. Thenard managed in 1818 to obtain hydrogen superoxide with the aid of barium superoxide.

Of their other collaborations one should mention their procedure for the elementary analysis of organic matters, using potassium as oxidizing agent. Thenard also worked on fatty acids, various kinds of ethers, gallnuts, etc. He improved the manufacture of white lead and developed an analytical test of aluminum compounds by heating with cobalt nitrate (Thenard's blue).

Amadeo Avogadro, Count of Quaregna (1776-1856, professor at the Lycee of Vercelli, from 1820 at Turin) assumed on the basis of these regularities in 1811 that the various gases in equal volumes under the same external conditions (pressure and temperature) contained the same number of molecules. Three years later, the same view was voiced by André Marie Ampère (1775-1836), physics professor in Paris. This "Avogadro law" or "Avogadro hypothesis" made the behavior of gases comprehensible with a single stroke. All the same, it received scant attention at first and it took many years before it became one of the most important foundations of chemistry and physics.

When exact determinations of atomic weights gave in most cases integral multiples of the weight of hydrogen, the English physician William Prout (1786-1850) published, at first anonymously, the hypothesis that all elements were composed of hydrogen as primary substance (1815). Three years later, Johann L. G. Meinecke (1781-1823), physics professor at the Cassel Engineering School (later at Halle University) independently developed the same view in Germany. The "Prout hypothesis" was later abandoned with

finer determinations of atomic weights; but after a century of varied fate it was brilliantly confirmed by the insights of nuclear physics into neutrons and protons as building materials of elements.

### *3. Discovery of new elements and further development of quantitative method.*

Little more than two dozen elements were known at the time when Scheele died (1786) and Lavoisier developed his oxidation theory. But at the turn of the century chemistry was enriched by the discovery of a large number of new elements. One of the most successful of the discoverers was Martin Heinrich Klaproth (1743-1817).

Klaproth was born at Wernigerode in the Harz Mountains as the son of a tailor. He chose the pharmaceutical career and served as apprentice and assistant at Quedlinburg, Hanover, Berlin and Danzig. In Berlin he studied chemistry, especially analytical, under Pott and Markgrafe. He also became a close friend of Valentine Rose the Elder (1736-1771) who owned the "Swan" pharmacy and discovered the "Rose metal," an alloy of lead, bismuth and tin. After Rose's death, Klaproth managed his pharmacy and also took over the education of his young son, Valentine Rose the Younger (1762-1807). After the latter's untimely death, Klaproth educated his two sons, Heinrich (1795-1864, later chemistry and pharmacy professor) and Gustav (1798-1873, later mineralogy professor in Berlin), and then acquired his own pharmacy. In 1797 Klaproth became chemistry teacher at the Artillery School and in 1810 he became chemistry professor at the newly opened Berlin University. But within three years the 70-year-old man suffered a stroke, from which he never recovered. His last four years were spent in enforced idleness.

Klaproth's services to analytic chemistry were such that Berzelius called him "Europe's greatest analytical chemist." It was he who coined the German words "Kali" and "Natron" (caustic potash and caustic soda). He improved silicate fusion by potassium melt in a silver crucible; he also introduced the careful drying and heating of the precipitates and the custom of giving not only the final results but also the individual weights of the precipitates.

His careful work enabled him to discover a number of new elements. In pitchblende, hitherto held to be a zinc ore containing iron and wolfram, he discovered in 1789 an unknown element which he named "uranium" in honor of Frederick William Herschel's discovery of the planet Uranus in 1781. He could hardly foresee that he discovered the "ancestor of the elements" whose hidden nuclear energy would end World War II 150 years later. Others, including Berzelius in 1823, confirmed Klaproth's findings. But in 1841 Eugene Melchior Peligot (1811-1899, professor and minting expert in Paris) proved that Klaproth's reduction had merely led to the protoxide, from which metallic uranium had to be obtained by further reduction.

In the year he discovered uranium Klaproth found in zircon from Ceylon an unknown component which he called "zirconia" (zirconium earth). Only 35 years later, in 1824, Berzelius was able to obtain from it metallic zirconium. In 1793 Klaproth proved the existence of an unknown ore in a mineral found by Adair Crawford (1749-1795, chemistry professor at the Woolwich military academy) near the Scottish village of Strontian. Klaproth named this ore, which had been also and independently found by Thomas Hope (1766-1844, chemistry professor at Edinburgh), "strontia" (strontium earth). Metallic strontium was obtained electrolytically by Davy in 1808, but it was only in 1855 that Bunsen obtained it in a really pure state.

In investigating rutile in 1795, then considered a kind of garnet or tourmaline, Klaproth obtained a "white earth," the oxide of an unknown metal which he baptized "titanium" after the "original sons of the earth." He also proved that it was the same element as the English country priest William Gregor (1762-1817) found in 1789 in an ore occurring at Menachan in Cornwall. Berzelius obtained metallic titanium by melting fluoride with metallic potassium, but only Woehler in 1857 recognized it as such.

In 1797 Klaproth discovered in Siberian crocoite an unknown element which he called "chromium" from the lively color of its compounds (the Greek "chroma" means color). The discovery was simultaneously made by Louis Nicolas Vauquelin (1763-1829), a pupil and successor of Fourcroy, later chemistry and pharmacy professor in Paris and a very successful organic and inorganic chemist. Klaproth confirmed the discovery, also made by Vauquelin in the same year, of beryllia in the long-known mineral that gave its name to eyeglasses ("Brillen" in German). Beryllium had hitherto been considered a mixture of alumina, lime and silica. Metallic beryllium was obtained only in 1828 by Woehler and by Antoine Alexandre Bussy (1794-1822, chemistry professor at the Paris Ecole de Pharmacie) by the same method as aluminum.

But this was not all. Already Franz Joseph Muller Baron von Reichenstein (1740-1825, administrator of Transylvanian mines and foundries in Vienna) had suspected that Transylvanian gold ore contained a hitherto unknown element. In 1798 Klaproth was able to prove its existence, also in sylvanite. He named the new element "tellurium" after the "old mother earth" (Latin "tellus").

The Finnish chemist Johan Gadolin (1760-1825) found in 1794 an unknown earth in the mineral he discovered in the same year at Ytterby in Sweden and named after him

"gadolinite." The Swede A. G. Ekeberg (1767-1813) investigated it again in 1798 and called it "yttria." Both Klaproth and Vauquelin confirmed his finding in 1800 by detailed analysis. The new element yttrium was obtained by Woehler in 1828 by melting with metallic potassium. In 1803 Klaproth proved the existence of a new earth in another Swedish mineral hitherto believed to be scheelite. He called the earth "ochroite" because of its pale brown color ("ochros," Greek for "pale"). Berzelius and Hisinger simultaneously made the same discovery and called the new element "cerium."

Among Klaproth's other scientific achievements are his proof of "Vegetable alkali" (potassium) in feldspar and the discovery of mellitic acid  $C_6(COOH)_6$  in the "honey stone" occurring in lignite mines. He helped the development of chemistry in Germany by being one of the first to support Lavoisier's new theory in a lecture he gave to the Prussian Academy of Sciences in 1793. Of his works the most noteworthy are his "Contributions to the chemical knowledge of mineral bodies," in five volumes (1795-1810), which was for a considerable time the basis of exact analysis of minerals.

Other chemists also found new elements in the great spurt of the turn of the century. Four other elements were found by treating platinum ore residues with aqua regia. Smithson Tennant (1761-1815, a pupil of Black who became chemistry professor at Cambridge after considerable travels abroad) discovered in 1802 iridium (from the Greek "iris," rainbow, because of its multicolored compounds) and in 1804 osmium (from the Greek "osme," smell, because of the peculiar smell of its volatile oxide). Two others were discovered by W. H. Wollaston in the same year 1804: palladium (named after the small planet Pallas discovered by Olfers in 1802) and rhodium (from the Greek "rhodon," rose, because of the reddish color of its acid salt solutions). The

fifth platinum metal, ruthenium, was discovered only 40 years later (1845) by Carl Claus.

The next wave of discoveries was due to electrochemistry which rapidly developed at the turn of the century. It was started by the discovery of the Bologna anatomy professor Luigi Galvani (1737-1798) in 1780 that frogs' legs twitched when touched with two linked wires of different metals, though this discovery was properly interpreted only by the Pavia physicist Alessandro Volta (1745-1837). It was Volta who set up in 1793 the electromotive series of metals. In 1798 Johann Wilhelm Ritter (1776-1810, at that time a student at Jena, later professor at Munich Academy, who discovered the photoelectric effect of ultraviolet light in 1801) declared that Volta's electromotive series coincided with the sequence of metals in their relationship to oxygen and in the mutual precipitability of their solutions. "The announcement that the system of chemistry would turn into that of electricity and vice versa should surprise no one," he said. This statement made Ritter, as Ostwald said, the founder of electrochemistry. In 1800 Volta discovered his electric battery, consisting of layers of pairs of copper and zinc plates separated by felt disks saturated with diluted sulfuric acid. It was the first apparatus to produce electric currents of some strength. This exciting discovery greatly fostered the experimental natural sciences. In the very year of its discovery it was used to decompose water into hydrogen and oxygen. This was done by William Nicholson (1753-1815, businessman and hydraulic engineer in London) and Sir Anthony Carlisle (1768-1840, surgeon and anatomy professor in London). It had been done in 1789 by two Dutchmen, Joh. Rudh. Deiman (1743-1808, Amsterdam physician) and Adriaen Paets von Troostwijk (1752-1837, Amsterdam businessman), using frictional electricity. These and other electrolytical phenomena were in-

terpreted in 1805 by the twenty-year-old Baltic German, Theodor Baron von Grotthuss (1785-1822, private scientist and landed proprietor in Lithuania). He said that when electrical current passed through a solution there was an exchange of positive and negative electricity between individual molecules and that the particles set free were separated at the poles, while they continuously formed chains in the solution itself.

The new electrical aids to chemistry were brilliantly used by the youthful Humphrey Davy (1778-1829) whose discoveries earned him the title of "the most famous chemist of Europe."

Davy was born in simple circumstances: his father was a woodcarver at Penzance in Cornwall. He was apprenticed to a practicing physician and developed his great gifts for the natural sciences to the highest degree by continuous study. At 20 he started working at Dr. Beckdoes' "Pneumatic Institute" at Clifton near Bristol; it was there that he discovered the intoxicating effects of nitrous oxide ( $N_2O$ ) which was thence called "laughing gas." Within three years (1801) his abilities got him a post with the Royal Institution, founded by the philanthropist Count Rumford (1753-1814) in London. Here he had to lecture experimentally to educated laymen. He was such a success that he became a full professor within a few months. He soon moved in high society circles, became Sir Humphrey Davy in 1812 and married a rich widow, at whose wish he gave up his professorship. He travelled extensively with his wife in France and Italy. On the first of these trips he took young Michael Faraday as secretary and courier (1814). He carried chemical and physical apparatus in his luggage so he could perform experiments on his travels at a moment's notice. Because of overstrain he suffered several bodily and mental breakdowns. He died in Geneva on his way back from a journey to Italy,

this time without his wife, and was buried there. He was 51.

Davy's scientific achievements, which astonished the world, were obtained with the aid of the voltaic battery. He provided an explanation for the processes taking place between the copper and zinc plates and the acid or salt solution by combining Volta's contact theory with other people's chemical theory. By thoroughly purifying water and by using gold vessels instead of the then easily corrosible glass he proved that the electrical decomposition of water produced, not as others thought, alkali and acid but only hydrogen and oxygen. In further experiments with galvanic elements, which he tied together with wet strips of material, he observed the phenomenon later called the "ionic migration." Davy's achievements created such an impression that he received in 1806 Napoleon's prize for electrical discoveries, that had been granted five years before to Volta for his "column." But they were put into the shade by Davy's achievements in the following year (1807) when he separated by strong electrical current metallic sodium and potassium from melted alkalis. The surprising qualities of these metals, so different from others—they swim restlessly on water, set themselves aflame and disappear with a bright light and a loud noise—are symbolic of the character of the man who discovered them. But the names "sodium" and "potassium" that Davy proposed for them were accepted only in English. Ludwig Wilhelm Gilbert (1769-1824, physics and chemistry professor at Halle and Leipzig, editor of the "Annals of Physics") proposed instead "Kalium" and "Natronium," used in German—the latter abbreviated to "Natrium" by Berzelius. In 1808 Davy managed to obtain the alkaline earth metals calcium, strontium and barium, at first in the form of amalgams by using mercury electrodes. The magnesium obtained in the same way was still very impure; it was obtained in a pure state only in 1829 by



Liebig and Bussy. Davy did not succeed in obtaining a metal from alumina.

In 1810 Davy proved by experimental work with hydrochloric acid and its salts that the so-called "oxidized hydrochloric acid" could not be further decomposed and was therefore an element. He proposed for it the name "chlorine" or "chloric gas" (from the Greek "chloros," greenish-yellow). Germans preferred the simpler "Chlor," proposed by Gay-Lussac. The name "halogen" proposed by Johann Salomon Christoph Schweiger (1779-1857, professor at Erlangen and Halle, editor of the *Journal for Physics and Chemistry*) was given to the group of three elements after the discovery of iodine and bromine. Davy also discovered the explosive chlorine dioxide and obtained phosphorous tri- and pentachloride and phosphorous acid. Davy also proved that hydrofluoric acid, which already Ampère declared to be the hydrogen compound of an unknown element, was free from oxygen. But only Henri Moissan succeeded in obtaining free fluorine in 1886.

The soap and saltpeter manufacturer Bernard Courtois (1777-1838) discovered iodine in Paris in 1811. The new element, named from the Greek "ioeides" (violet blue) was obtained from a mother liquor of seaweed ashes, which was also investigated by Gay-Lussac. Davy, too, was attracted by the new discovery. During his stay in Paris (1813) he carried out experiments with iodine samples supplied to him by Ampère, partly in his travelling laboratory and partly in the laboratory of young Chevreuil. He obtained hydrogen iodide and also nitrogen iodide, with its explosive properties, that had been meanwhile discovered by Clement and Desormes. For all his social engagements Davy worked at such a speed that he actually beat his rival Gay-Lussac as regards publication.

Frequent fire damp explosions in English coal mines made

Davy invent in 1815 a safety lamp in which the light is separated from the outer air by a close-meshed wire-netting. This very beneficent invention made Davy very popular but involved him in a lengthy dispute about priority with George Stephenson (1781-1848), the inventor of the improved steam engine. In his investigations of combustion Davy also discovered the catalytic effect of heated platinum wires on combustible gas mixtures.

The further development of the quantitative method based on the atomic theory was due in the first place to a man who combined the talents of an excellent experimentalist, a theorizer, a teacher and an organizer that are only rarely found together. It was the Swede Joens Jacob Berzelius (1779-1848).

Berzelius was born at Waeversunda in East Gotland province in the house of his maternal grandparents. His father was a schoolteacher at Linköping. His parents died early (1783 and 1788) and young Berzelius had to earn his own living while still at school. By tutoring and working on the land he earned the opportunity to study medicine at Upsala where, as a "working student," he also became interested in chemistry. He overcame all difficulties by an iron discipline. After passing his state medical examination he was employed in 1802 by the Stockholm Surgical Institute as an "adjunct" without pay. The mine owner W. Hisinger (1776-1852), in whose house he lived, became his personal friend and scientific collaborator. By participating in an industrial undertaking Berzelius became involved in a heavy load of debt which he had to pay up laboriously over many years.

He became a professor in 1808, and a member of the Swedish Academy of Sciences in 1809 (he became its president the very next year and acted as its permanent secretary from 1818 onwards). He was ennobled when Bernadotte was crowned king of Sweden in 1818 and was granted

the title of baron in 1835. For all this he carried out his chemical investigations with an extraordinary diligence and he trained in his Academy laboratory eager young students, whose number was never more than two at a time, and who became capable scientists. Among them were the Germans Chr. Gottlieb Gmelin; Heinrich and Gustav Rose; Friedrich Woehler; and Gustav Magnus. Like many other experimentalists Berzelius was seriously injured in an explosion—it happened in 1809 when he was working with fulminating gold. His eyesight was affected and he had to spend several months in the dark. On several occasions (1818 and 1835) Berzelius paid for his perpetual overstrain with a complete bodily, mental and spiritual breakdown. He sought and found recovery in lengthy travels. At 56 he married a girl of 24. Finally, plagued by a heavy gouty illness, he died in full possession of his capacities, shortly before his 69th birthday.

Berzelius' scientific achievements embrace all branches of chemistry. In his case, too, they were initiated by the voltaic battery. As early as in 1802 he determined together with his friend and patron Hisinger that alkaline salts are decomposed in the passage of the electric current into acid and base. This finding became the basis of his electrochemical theory, developed in 1819, and of his dualistic system. He viewed electricity as the "prime mover" of all chemical processes and applied this view also to the atoms of elements which he conceived as electrically dipolar with—except for the neutral hydrogen—a preponderating positive or negative electrical charge. Corresponding to Volta's electromotive series he ordered the elements into an electrochemical series, from the most strongly electro-positive potassium over neutral hydrogen to the (then) most strongly negative element, oxygen. His dualistic system based on the dipolar principle was applied also to his views on chemical compounds. Unions

of oxygen with metals produce the basic oxides ( $K_2O$ ) ; with metalloids, the acid oxides ( $SO_3$ ) as compounds of the first order. Unions of basic and acid oxides produce neutral salts ( $K_2O$ ,  $SO_3$ ) as compounds of the second order. Unions of two salts produce double salts as compounds of the third order, e.g., alum ( $K_2O$ ,  $SO_3$ ,  $Al_2O_3$ ,  $(S_3O)_3$ ). This dualistic formulation of inorganic compounds was current for several decades.

The work of Wenzel and Richter aroused Berzelius' interest in the regularities of chemical proportions which, combined with Dalton's now publicized atomic theory, seemed to him to form the most important problem of chemistry. As already mentioned, he erroneously attributed the discovery of the neutrality law to Wenzel instead of Richter. He tried to produce experimental proof of the atomic conception of the observed quantitative regularities of chemical proportions. As he himself put it, he devoted to this task the greatest part of his life work. The "oxygen law" or regularity noted by him in 1810 that in salts the quantities of oxygen contents of acid and base relate to each other in a simple integral<sup>\*</sup> ratio made him refer the combining weights of various elements to oxygen, the "angle or central point of chemistry." He turned the combining weights into atomic weights by making the atomic weight of oxygen 100. After establishing the atomic weights of almost all the known elements (about 40) in several years' hard work, he published in 1818 his table of atomic weights, followed in 1826 by a second improved edition. The latter also included among the elements chlorine and nitrogen which were hitherto held by Berzelius to be oxygen compounds of unknown elements ("murium" and "ammonium" or "nitrium").

He now had to admit that there existed acids (hydrochloric acid) and bases (ammonia) that did not contain oxygen, a fact that could not easily fit into his strictly dualis-

tic system. Berzelius' atomic weights were universally accepted as valid because of the author's great reputation. All the greater was the sensation in 1840 when J. B. Dumas and J. Stas proved that there is a not inconsiderable error in the determination of the atomic weight of carbon (12.2 instead of 12.0). But this was the only error the master had made.

Berzelius later referred the atomic weights to the weight of hydrogen taken as unity. Since any change in the correct determination of the weight ratio of oxygen and hydrogen would make it necessary to re-calculate the atomic weights of most elements, an intermediary method has been used of late. While formally keeping hydrogen as unity, the atomic weight of oxygen is taken to be 16.0 which gives 1.008 for hydrogen.

Careful investigation of many natural substances made Berzelius discover new elements. At the very beginning of his scientific career (1803) he and Hisinger found an unknown "earth" in a mineral occurring at Riddarhytta and considered a kind of scheelite. They proved it to be the oxide of a metal which they named "cerium" in honor of the small planet Ceres discovered in 1801 by the Italian astronomer Giuseppe Piazzi (1746-1826). As already noted, Klaproth made simultaneously the same discovery in Berlin. In 1817 Berzelius discovered a new element in the mud of a lead chamber of a chemical work at Gripsholm in which he had a business interest. Because it was similar to the tellurium discovered by Klaproth in 1798 he called it "selenium" (from the Greek "selene," moon). In the same year his pupil Johan August Arfvedson (1792-1841) discovered a new element in the mineral petalite and later also in lepidolite and spodumene. It was named lithium, from the Greek "lithos," stone. Berzelius found it later (1825) in the mineral waters of Karlsbad, Marienbad and Franzensbad. In 1828 he discovered an unknown earth in a Norwegian

mineral. He named it "thorium" in honor of the Germanic god of thunder. Just as he had obtained silicium (1810), zirconium, titanium and tantalum (1824), hitherto unknown in free state—by the action of metallic potassium on the halides—so he obtained metallic thorium in 1826 (?). His pupil Nils Gabriel Sefstroem (1787-1845, professor at the Falun Mining Academy), visiting him for Christmas in 1830, experimented with a material obtained from Swedish bar iron. With his teacher aiding him, Sefstroem could prove the presence of a new metal. Berzelius named it "vanadium," after the Nordic goddess of beauty Vanadis, because of the beautiful colorings of its compounds. Friedrich Woehler missed making this discovery in investigating a lead ore from Mexico. He became ill of poisoning with hydrofluoric acid vapors, was unable to work for some time and let the matter drop.

When Berzelius received in 1812 a mineral collection from an English doctor as thanks-offering for chemistry lessons he was inspired to work out a more systematic classification of minerals. He proposed a classification according to chemical composition to replace that of the Paris mineralogist René Just Haüy (1743-1822), based on crystallic systems. Silica, hitherto treated like other "earths," he classified as an acid which combines in corresponding chemical proportions with various basic earths to form saltlike "silicates." The one-time mining engineer Johann Gottlieb Gahn (1745-1818), pupil of Bergman and friend of Scheele, befriended him and taught him many analytic procedures, especially the art of blow-pipe analysis, which Berzelius made even more exact for his investigations of minerals. He always carried a blow-pipe on his travels. When he met Goethe at Marienbad in 1822 and the two made a geological excursion to Kammersbuehl near Eger, Berzelius demonstrated his skill in blow-pipe blowing.

Berzelius achieved great things as an analytical chemist. He had to clean most of the chemicals himself to obtain exact determinations of their atomic weights. He ordered the manufacture of clean white blotting paper, which became very generally used as "Swedish filter paper." Most of the apparatus still used in chemical laboratories was originated by him: glass funnels, beakers, washing bottles, etc. One might say that he transformed the alchemists' kitchen into a modern laboratory. For heating he used a very adequate spirit burner, later used as "Berzelius lamp" in all laboratories, until the coming of the lighting gas replaced it by the "Bunsen burner." He replaced the clumsily sewn leather tubes by rubber tubes and altogether started quite a few other improvements in laboratory equipment.

Another great service of Berzelius to chemistry was his introduction of generally acceptable chemical symbols. In 1813-4 he dropped Dalton's circles, dots and lines in favor of simply taking the first letter of the Latin name of each element to which, if necessary, the second was added. At first he still used dots over the symbols of other elements to indicate the oxygen atoms and dashes to indicate double atoms. But he soon developed the symbols for chemical formulas that are still universally used. They could also be used for organic compounds (Berzelius discovered by combustion analysis to his great surprise that the law of chemical proportions applied also to their composition).

Another thing Berzelius did for chemistry was to view certain phenomena observed with different materials under a common denominator and to introduce new names for them. In 1830 he discovered that two organic acids with different properties, tartaric acid and racemic acid, had the same percentage composition. Berzelius introduced for this phenomenon the name "isomerism" and further distinguished between "metamerism" and "polymerism." He

called in 1841 "allotropism" the appearance of elements in different manifestations. He coined the term "catalysis" for mysterious acceleration of chemical processes by the presence of relatively small quantities of substances that do not seem to take part in these processes. This has been observed in a number of different cases, and in 1836 Berzelius wrote a book about it. (It is worth noting that the word catalysis was already used in 1597 by Libavius in his book "Alchymy.") The new term applied to the oxidizing processes noted by Humphrey Davy in incandescent platinum wires and in the platinum black obtained in 1817 by his nephew Edmund Davy, chemistry professor at Cork and Dublin; also to the oxidation of alcohol into acetic acid achieved by Doebereiner in 1821 and his inflammation of hydrogen in air (Doebereiner's lighter, 1823); finally the method of rapid manufacture of vinegar by fermentation discovered in 1823 by Karl Sebastian Schuetzenbach (1793-1869), a chemist at Baden-Baden. Berzelius also viewed the enzymes and ferments which caused biological-physiological phenomena as "catalyzers" (biocatalyzers). He prophetically foresaw the great part now played in industry by catalyzers.

Berzelius also contributed to the reformation and organization of chemistry by his writings. He was the first to use the term "organic chemistry" for chemical processes taking place in living organisms (in a textbook, "Animal chemistry," he wrote for his medical students in 1806). However, the German romantic poet Friedrich von Hardenberg (1772-1801) who wrote under the pen name of "Novalis" already spoke of "organic chemistry" in the same sense in 1800. Gradually this name was applied to the chemistry of carbon compounds. The six volumes of Berzelius' great "Manual of chemistry"—the last three volumes subtitled "Manual of organic chemistry"—appeared in 1808 through 1830. Friedrich Woehler translated it into German and there were trans-



lations into other languages. From 1821 Berzelius regularly published his "Annual Reports on the Progress of the Physical Sciences," containing his critical appreciation on the work done in all areas of chemistry. The younger scientists were thus given the critical opinions of the master.

Michael Faraday (1791-1867) greatly helped the further progress of electrochemistry and the quantitative method.

He was born in London, the son of a farrier, in very modest circumstances. He worked his way up from newspaper boy and bookbinder's apprentice to one of the most famous of all scientists. In his immense zeal for learning he not only read all the books he had to bind but also frequented scientific lectures in the evenings. He was so enthusiastic about Davy's experimental lectures at the Royal Institution that he wrote them down, illustrated them with beautiful drawings and sent them to Davy with the request to make him his laboratory assistant. Davy granted the request and soon recognized him as a very capable and valuable collaborator. As already mentioned, Faraday accompanied Davy on his 1813 journey. He patiently bore Davy's haughty treatment in the interest of extending his scientific knowledge. In 1824 he became a member of the Royal Society, though against the will of Davy who became jealous of his successful rival as his own strength began to give way. But Davy could not prevent Faraday from becoming his second successor as professor at the Royal Institution. Faraday belonged, like his father, to the strict "Sandemanian" sect and remained a simple and modest man to the end of his days. Because of constant overwork he twice suffered, like Davy and Berzelius, a heavy collapse, in 1840 and 1843. He particularly suffered from a great weakness of memory which finally made any kind of scientific work impossible for him. He bore his fate patiently and spent the last six years of his life in a house

given to him by Queen Victoria's husband, Prince Albert.

Among the great number of Faraday's scientific works comparatively few are chemical. At the very beginning of his scientific activity he carried out some chemical investigations: he discovered carbon chloride compounds and separated two isomeric naphthalene sulfonic acids. In 1825 he made two important discoveries about lighting gas which at that time in London was not piped through to the consumers but supplied in a compressed state in great iron flasks ("gas bombs"), as with propane heating today. He found a liquid hydrocarbon, butylene,  $C_4H_8$ , with the same percentage composition ( $C:H=1:2$ ) as the "oil forming gas," ethylene,  $C_2H_4$ . He also found a hydrocarbon of very different properties, which ultimate analysis proved to have the ratio of  $C:H=1:1$ . This was benzene,  $C_6H_6$ , which was to become so important later.

Faraday's interest then turned almost entirely to the study of electrical phenomena and it was here that he made his fundamental observations. He proved that there was only one kind of electricity and that frictional and galvanic electricity were identical. In 1831 he discovered the electric and electromagnetic induction currents (lines of force). In 1834 he proclaimed two important natural laws: first, that the quantity of matter separated by the electric current is always proportionate to the quantity of electricity used, and second, the so-called "law of fixed electrolytic action," according to which the same quantity of electricity passing through different salt solutions always separated equivalent quantities of the various components. This "Faraday's Law" played a great part in the further development of chemistry. In addition to important physical observations it is also worth noting that Faraday coined a clear and systematic nomenclature for electrical processes and apparatus. He created words like electrode, electrolyte, anode and cathode, anion

and cation.

Faraday's writings mostly appeared in the Transactions of the Royal Society. In 1827 he published "Chemical Manipulations" as a separate book. A small popular brochure, "The Natural History of a Candle," was extremely popular and was translated into many languages.

Germany produced in the first half of the 19th century several capable chemists of whom Eilhard Mitscherlich (1794-1863) will be dealt with first.

Mitscherlich was born at Neurode near Jever in Oldenburg. He came to chemistry in a strange way. He studied Oriental languages in Heidelberg and Paris and hoped to go to Persia with a mission that Napoleon planned to send there. These hopes were shattered by Napoleon's defeat at Leipzig. His hopes to get a travelling scholarship in other ways were also disappointed. He then decided to study medicine, which would enable him to go to the Orient as a ship's doctor. He started to study at Goettingen in 1817. Professor Friedrich Stromeyer (1776-1835), who was the first German professor to start practical teaching in the laboratory and who had just discovered cadmium (1817) in a pharmaceutical zinc preparate, persuaded him to study chemistry instead. He obtained a doctorate at Goettingen with a study of Persian texts and moved in 1818 to Berlin University. There, in the laboratory of the botanist H. F. Link (1767-1851), he made his great discovery of isomorphism. Berzelius, who came to Berlin to become Klaproth's successor in 1819, proposed that the chair be given to Mitscherlich instead and offered to give him the required training. Mitscherlich went to Stockholm for two years' training, then returned to Berlin to become extraordinary professor in 1822 and ordinary professor in 1825. He was a professor of Berlin University for 42 years, until his death.

Mitscherlich's most important discovery was his first.

While working with phosphates and arsenates of potassium in 1818 he noted that both salts crystallized in the same crystal form and the crystals of one salt continued to grow in solutions of the other. He noted the same behavior in other salts e.g. sulfates of magnesium and zinc, bivalent iron, double salts of alum, etc. A couple of years later (1821) he discovered dimorphism in calcspar and aragonite which had the same chemical composition but different form (hexagonal and rhombic). He observed the same phenomenon with sulfur and other minerals, and it could be developed into the concept of polymorphism.

Isomorphism and the law of constant atomic heats of elements in a solid state (the product of atomic weight and specific heat is constant:  $\Lambda C = 6.4$ ) proved of special importance for the determination of atomic weights. The law was discovered about the same time (1819) by Pierre Louis Dulong (1785-1838), a Paris professor who discovered nitrogen chloride in 1811 and lost an eye and several fingers in an explosion, and Alexis Thérèse Petit (1791-1820), who was also a professor in Paris.

Berzelius saw himself forced to add halved values of atomic weights for a number of elements: Fe, Al, Cr, Cu, Sn, Pb, Zn, Mn, Mg, Ca, Sr, Ba, Na, K, etc. The new values are given in the second table of atomic weights that he published in 1826. In 1831, Franz Neumann (1798-1895), physics professor at Koenigsberg, and Henri Victor Regnault (1810-1878), chemistry professor in Paris and director of the Sevres porcelain works, extended the law of constant atomic heats by discovering that the molecular heats of analogously composed compounds had the same value.

Among Mitscherlich's many other investigations the following are worth mentioning: proof of phosphorus by volatilization with water vapor (shining ring in the cooling

tube), clarification of the various oxidation stages of manganese ("the chemical chameleon"), determinations of the density of gases and vapors, measurements of crystal angles, production of benzene from benzoate of lime and of various benzene derivatives—nitrobenzene, azobenzene, benzenesulfonic acid, etc. He cleared up the formation of ethyl ether from alcohol under the action of small quantities of sulfuric acid and the splitting of cane sugar into grape and fruit sugar ("invert sugar"). These processes proved important examples for Berzelius' catalysis theory and so did conversion of starch into sugar by heating with highly diluted sulfuric acid, discovered already in 1811 by Gottlieb Sigismund Kirchhoff (1764-1833), director of the Imperial Pharmacy in Saint Petersburg, who came originally from Mecklenburg. Mitscherlich helped the investigation and production of sugar by constructing an adequate polarization apparatus and by his thorough investigation of the "Fehling solution," a solution of alkaline copper and Seignette salt, created by Hermann von Fehling (1812-1885, professor at Stuttgart).

Mitscherlich's "Manual of Chemistry," published in 1829-30 and republished many times, was praised by Liebig as "the crown of all chemistry manuals." But for all his scientific fame he was unable to persuade the Prussian Ministry of Education to set up a teaching laboratory in Berlin University. Berlin and other Prussian universities remained in this respect for several decades behind Goettingen, Giessen and Marburg.

#### *4. The three great German chemists: Liebig, Woehler and Bunsen.*

Of the three great scientists who boosted chemistry in Germany, we will start with Justus Liebig (1803-1873).

He was born at Darmstadt on May 15, 1803, the son of a druggist. His chemical talents manifested themselves quite early with independent experiments—with fulminating silver. Like Scheele, he chose the pharmaceutical career. He went to the Gymnasium until the last grade but one and then became at 16 apprentice in a Heppenheim pharmacy located in the Bergstrasse. But he was soon dismissed as incompetent by his master, who used as the pretext an explosion which occurred one night when the boy experimented in his room, and he returned, deeply disappointed, to his parents' home. There he continued his studies with books he obtained from the grand duke's library until his father finally made it possible for him to study chemistry at a university and thus fulfilled his dearest wish. In the fall of 1820 he went to Bonn University, opened the year before. Chemistry was taught there by Karl Wilhelm Kastner (1783-1857), a man who had the reputation of being the best German chemist, for whose services the various universities competed. Next year Kastner moved to Erlangen, and Liebig followed him in the hope that Kastner would explain to him, as he had promised, the secrets of analytical procedure. But Liebig was deeply disappointed. He tried instead to fill the gaps in his general culture and frequented the lectures of the famous natural philosopher Schelling (1775-1854), whose teachings he later strongly condemned as "scientific plague." An intimate friendship with the poet August Count von Platen (1796-1835) proved shortlived. He was lucky to escape arrest as a member of a suspect regional students' association. In March 1822 he returned to the parental home and a grand ducal scholarship enabled him to continue his studies in Paris. There he listened to famous scientists like Gay-Lussac, Thenard, Laplace, Cuvier, etc., and continued his investigation of fulminic salts in the laboratory of Vauquelin. A report on his work, read to the Academy by

Gay-Lussac, drew Alexander von Humboldt's attention to the capable young scientist, who had meanwhile obtained his Ph.D. at Erlangen "in absentia" (June 21, 1823.) On Humboldt's recommendation Gay-Lussac admitted Liebig to his laboratory and participated in his investigations.

It was also Humboldt who, by intervening with the grand duke, made it possible for Liebig to become extraordinary professor at Giessen at the age of 21, shortly after his return from Paris in March 1824. He lectured with great enthusiasm and carried out practical work with his students in a laboratory set up in the guard room of an old barracks. The ordinary chemistry professor, W. L. Zimmermann (1780-1825) soon had no students left and when he died in a bathing accident next summer—probably a suicide—Liebig succeeded to his post. Liebig now had at his disposal a large laboratory with a lecture room. It was here that he trained young chemists who flocked to him from inside and outside Germany as independent investigators and thus really started the scientific teaching of chemistry. He enjoyed great fame, as both teacher and investigator. The grand duke ennobled him in 1845 with the title of baron. After rejecting offers from other universities he accepted a specially honorable one from Munich in 1852 under the explicit condition of being entirely freed from laboratory teaching which had consumed his strength through his enthusiasm. From now on he only lectured and wrote. His lively and sanguine character was not afraid of stirring up any amount of wasps' nests—he was engaged in many a hard controversy. He became president of the Bavarian Academy of Sciences and enjoyed an international fame. On April 18, 1873, his very successful life came to an end.

Liebig's scientific work started with the explosive compounds with which he had worked—or rather played—as a boy. The ultimate analysis of fulminating silver which he

carried out in Gay-Lussac's laboratory in 1823 produced, to his great surprise, the same results as Woehler had obtained shortly before with cyanide of silver. It seemed to him quite impossible that two chemical compounds with opposite properties should have the same composition. And so he questioned Woehler's results, especially since his own analysis of silver cyanide produced different values. But when he repeated his analysis with a quite pure prepare he had to confirm Woehler's findings. It was a particularly striking example of the phenomenon baptized "isomerism" by Berzelius. This scientific controversy between the two young chemists had another important consequence for chemistry: following a meeting the two became excellent friends. Their friendship lasted undisturbed till Liebig's death and proved very beneficial to chemistry.

Among the many analyses carried out by Liebig at the beginning of his academic career was that of the Kreuznach brine and mother lye. By the action of chlorine he obtained, besides iodine, a brown fluid which he held to be a compound of iodine and chlorine. When the French pharmacist Antoine Jerome Balard (1802-1876, professor at Montpellier and Paris) announced next year (1826) his discovery of bromine in the water of the Mediterranean, Liebig was much vexed to discover what he had missed. This "missed discovery" bothered him all the more because he never had any other chance to discover a new element.

Liebig served organic chemistry especially by improving the method of ultimate analysis. Lavoisier's first experiments in this direction were continued by Gay-Lussac and Thenard and were particularly improved by the use of copper oxide as oxygen transmitter (1815, simultaneously recommended by Doebereiner). Berzelius caught the water obtained in the combustion with solid calcium chloride and the carbon dioxide thus formed with solid caustic potash



and weighed them. Liebig gave the combustion tube, that Berzelius had moved from a vertical into an almost horizontal position, its "bayonet" form. In 1831 he introduced the potash apparatus, filled with a caustic potash solution, to catch the carbon dioxide. Its three spheres were worn as an emblem by Liebig's students. In 1831 he performed the determination of nitrogen separately from that of carbon and hydrogen. His method—passage of combustion gases over incandescent copper and catching the reduced nitrogen over caustic potash solution—has become generally used in the form indicated by Dumas.

Another method to determine nitrogen was offered in 1841 by Heinrich Will (1812-1890), a pupil of Liebig's who took his Giessen post in 1852, and Franz Varrentrapp (1815-1877), professor and minting specialist at Braunschweig. 1839-1841 at Giessen. It consisted in heating with soda lime and catching the thus developed ammonia with hydrochloric acid; it could not be used for nitro compounds. A third method, very widespread in physiological and nutritional chemistry, was developed in 1833 by the Danish chemist Johan Kjeldahl (1849-1900). It consists in heating with concentrated sulfuric acid with addition of  $\text{KMnO}_4$ ,  $\text{CuO}$  or suchlike in a "Kjeldahl flask," until cleared; then the  $\text{NH}_3$  developed is distilled away in the acid applied. This method cannot be used for nitro and cyanogen compounds nor for quinoline and pyridine derivatives.

We can mention here only the most important of the many investigations carried out by Liebig, mostly with the aid of his students. In 1831 he discovered, in the action of chlorine on alcohol, chloral ( $\text{Cl}_3\text{CHO}$ ) and chloroform ( $\text{CHCl}_3$ ), simultaneously with the Frenchman E. Soubeiran (1797-1858). He then worked on aldehyde, already observed by Scheele in 1774 and investigated by Fourcroy and Vauquelin in 1800. He determined its chemical charac-

ter as an oxidation product of alcohol (alcohol dehydrogenatus) and showed in 1835 that there existed a whole class of such compounds. In 1832 he worked with Woehler in his Giessen laboratory on the oil of bitter almonds and benzoic acid. "Benzoyl" ( $C_6H_5CO$ ) could be passed unchanged, like an element, from one compound into another. Together with Gay-Lussac's cyanogen it was a further important example for Berzelius' radical theory. Liebig found similar conditions in his investigation of "the constitution of ether and its compounds" of 1834. He named "ethyl" the  $C_2H_5$  group which appears unchanged in most varied compounds. This radical was also contained in the thioalcohol "mercaptan" ( $C_2H_5SH$ ), discovered in 1833 by the Copenhagen professor Will. Christopher Zeise (1789-1847), and many other organic compounds. Liebig viewed organic chemistry as "the chemistry of composite radicals." But other preoccupations made him abandon more and more the radical theory in the strict form that Berzelius gave to it. He also agreed to make another investigation together with Woehler: that of uric acid (1837) which they, however, carried out separately. It was, of course, impossible at the time to clear up its constitution.

Investigations of polybasic organic acids (1839) led Liebig to clarify the general concept of acids. The old idea that "one atom (i.e., molecule) of base" always corresponded to "one atom of acid" had to be given up. Examples of polybasic acids are sulfuric, arsenic and phosphoric acids in inorganic chemistry and tartaric, malic and tannic acids in organic. Liebig gave the definition that is still valid today: acids are hydrogen compounds whose hydrogen can be replaced by metals with formation of salts. The difference between acids that contain and do not contain oxygen thus disappears. For it is not oxygen that is the characteristic component of acids but hydrogen. "Oxygen" is, indeed, a

misnomer; the name should have been given to hydrogen. This idea of Davy's was completed by Liebig who thus finally clarified the concept of acid, basic and neutral salts.

Liebig tried to explain vegetable metabolism through detailed investigation of vegetable ashes. The "humus theory," then current in agriculture, assumed that plants were chiefly nourished by the humus contained in the soil and completely neglected the soil's mineral components. Liebig emphasized instead the fact, recognized already by Priestley and the Dutch physician J. Ingenhouss (1730-1799) that plants take their carbon not from the soil but from the slight (0.03%) carbon dioxide content of the air. His analysis of vegetable ashes proved that the mineral components required for plant growth—especially potassium, phosphorus and nitrogen—are being constantly removed from the soil. Since the supply of natural manure is insufficient to cover the needs of cereals and other farm produce, agricultural soil becomes steadily more impoverished. This was recognized in agricultural practice with the introduction of the three fields system, with its unploughed fallows. Liebig started an experimental field and demonstrated that the yield of agricultural soil can be substantially increased by the use of artificial mineral manures. Such experiments had already been made by Palissy in the 16th century and Glauber in the 17th. Liebig is the great reformer of agricultural methods, together with Albrecht Thaer (1752-1828), originally physician at Celle and then professor of agriculture in Berlin, who, indeed, started from quite different assumptions. Liebig is the founder of agricultural chemistry and his advocacy of mineral manures, which was only gradually heeded, proved of immense economic benefit.

These studies led Liebig to occupy himself with animal and human physiology, metabolism and nutrition. He pointed out that foods, in addition to organic components

required as building and combustion materials, contained nutritive salts and stimulating extractive materials. The meat extract prepared by him was manufactured from 1862 on a factory scale in Uruguay, the center of a great cattle area. "Liebig's meat extract," sold in cans bearing Liebig's name, made him especially popular.

Liebig was a very prolific writer. From 1832 he published the "Annals of Pharmacy," then from 1840 together with Woehler the "Annals of Chemistry and Pharmacy" now known as "Liebig's Annals." In 1842 he published, with some collaborators, the "Pocket dictionary of pure and applied chemistry" and after Berzelius' death in 1848 Liebig took over his "Annual Reports on the Progress of Chemistry." But he published on a popular as well as theoretical level, with aim of teaching and clarifying. He wrote the ruthlessly critical "On the state of chemistry in Austria" of 1838 and "On the state of chemistry in Prussia" of 1840, without, however, achieving any improvement of the conditions prevailing in the universities. But his "Organic chemistry applied to agriculture and physiology" (1840), "Organic chemistry as applied to physiology and pathology" (1842) and especially his "Chemical Letters" (1844, many re-issues) had very fruitful effects in cultural circles.

But Liebig's greatest services to chemistry were as teacher. Though some universities like Freiberg, Goettingen, Landshut, Jena and Breslau had provisions for practical laboratory work, Liebig was the real founder of scientific laboratory teaching. He trained his students in scientific thinking and turned them into independent investigators. He devoted himself to this task with all his fiery nature until he had to give it up, totally exhausted, 25 years later. His pupils were numerous in all civilized countries.

Next to Liebig, Friedrich Woehler (1800-1882) was the chief German chemist of his time.

He was born as a "refugee child" at Eschersheim near Frankfurt on July 31, 1800. His father, who was in charge of the horses of Crown Prince William of Hesse (later Elector William II), came to blows with his master and had to flee from his country. His pregnant wife found a refuge with the village minister of Eschersheim, belonging to the free city of Frankfurt, and there gave birth to the child. The father soon got a new job of caring for the horses of the Duke of Meiningen and was later put in charge of the Meiningen theater. In 1806 he acquired the property of Roedelheim near Frankfurt and in 1812 he moved to the city itself. His philanthropic activities were such that a street, a foundation and a school were named after him. Young Woehler grew up in the free city, educated at first by his many-talented father and then by excellent school-teachers. He early occupied himself with chemistry—he produced by himself the two elements discovered in 1817, selenium and cadmium—but he went to Marburg in 1820 to study medicine. Since there was no university laboratory at Marburg he carried out his experiments in his small room—to the great distress of his landlady. He experimented with cyanogen compounds and discovered cyanogen iodide and the curious phenomenon of "pharaoh's serpent" (burning mercury thiocyanide). Later he could work at Heidelberg with Leopold Gmelin (1788-1853) in his private laboratory. He became a doctor of medicine in September, 1823, with a dissertation on the "Conversion of substances in human urine"; but soon gave up the idea of practicing medicine and devoted himself entirely to chemistry. Gmelin made him go first to Stockholm to study under the great Berzelius.

As an old man, Woehler told the story of his adventurous journey to Stockholm and his study under Berzelius from the fall of 1823 to summer 1824, in "Recollections of a young

chemist," published in the Transactions of the German Chemical Association of 1875. He then returned to his parents' home at Frankfurt to prepare for an academic career when he was offered a post at the newly founded municipal technical school in Berlin. It was here that he made his two great discoveries that gave him scientific fame. He exchanged his Berlin post for a similar one at Cassel in 1831 and five years later became Stromeyer's successor in his Goettingen chair. There he was active as teacher and investigator till his death on September 23, 1882.

Woehler started his career as investigator, curiously enough, with a compound that not only has the same constituent elements (C, H, O, N) as that which occupied young Liebig's attention, but even had the same percentual composition. It is stranger still that the quite different properties of the two isomers mirror the two quite different characters of the two investigators. While the fiery Liebig plagued himself with the explosive fulminate of silver, the sober Woehler thoroughly investigated the harmless and quite unexplosive isocyanide of silver. Woehler's analytical formula  $\text{AgCNO}$ , whose correctness was prematurely challenged by Liebig, proved to be the right one for both compounds. These investigations, carried out by Liebig in Paris and Woehler in Stockholm, are important not only as an example of the phenomenon of isomerism but also as the link that led to the intimate friendship of these very different men. In his Stockholm experiments of 1823/4 Woehler treated liquid ammonia with cyanogen gas and obtained in addition to ammonia cyanide (and a dark coal-like by-product) ammonia oxalate, whose true nature he recognized only four years later.

It was at the laboratory of the Berlin technical school that Woehler made in 1827 his great chemical achievement that had been attempted in vain by Davy and the Danish

professor Hans Christian Oersted (1777-1851), the discoverer of electromagnetism in 1820; the production of metallic aluminum. Woehler managed it by treating the aluminum chloride, obtained by Oersted, with metallic potassium.

The discovery created a sensation but had at first no industrial consequences. The light metal remained very costly and it was not until the French chemist Henri Sainte-Claire Deville (1818-1881) got hold of Woehler's discovery in 1854 and offered an improved method of treating a mixture of sodium and aluminum chloride with sodium, that it could be produced in any quantity. In 1855, aluminum was the sensation of the Paris Universal Exposition: it was called "silver made of clay" and cost about 1000 francs a kilogram. A special medal was coined bearing on one side the face of Napoleon III and on the other that of Woehler and the date 1827. Both Woehler and Sainte-Claire Deville received the Officers Cross of the Legion of Honor. Even after Bunsen showed in 1854 that metallic aluminum could be obtained from melted aluminum-sodium chloride through the action of an electric current, it was a whole generation until the electrolytic method was started in 1888. By using water power (e.g., the Rhine falls at Schaffhausen) and the minerals cryolite ( $\text{Na}_3\text{AlF}_6$ ) and bauxite ( $\text{Al}_2\text{O}_3$ ), the industrial production of aluminum became at last a reality and the era of light metal technology was inaugurated.

In the next year, 1828, Woehler used the method with which he obtained aluminum to discover metallic beryllium and yttrium.

1828 was also the year of Woehler's second great discovery, which contributed even more to his fame. He was carrying on his earlier experiments with hydrocyanic acids and was trying to obtain ammonia (iso)cyanide by converting silver (iso)cyanide with ammonia chloride. He

found to his great surprise that an evaporation of the solution produced crystals of urea ( $\text{CO}(\text{NH}_2)_2$ ). His revered teacher Berzelius had declared shortly earlier that man would never be able to produce artificially the chemical compounds formed in living organisms; "vital force" was needed for that. But now the synthesis of an organic matter had been performed in a laboratory and the sensation was immense. Woehler himself did not at first draw any far-reaching consequences from his discovery. And yet he became the founder of synthetic organic chemistry: not indeed in Berlin in 1828 but four years earlier, at Stockholm, when he obtained, by the action of cyanogen on ammonia, ammonia oxalate in addition to then-still-unrecognized urea. But oxalic acid was not considered an "organic" acid at the time because its salts contained oxygen and carbon but no hydrogen.

In the summer of 1832 Woehler accepted Liebig's invitation to come to Giessen to console his friend after the death of his young wife and to divert him by joint work. It was then that they undertook the work with the oil of bitter almonds and the radical of benzoic acid that made Berzelius salute it as "the dawn of a new day in organic chemistry." They also agreed on a number of other enterprises which they later carried out by correspondence.

Woehler's career as scientist lasted over half a century and touched upon almost all the areas of chemistry. His scientific results helped industry greatly though he was not directly concerned with industry. Of his inorganic achievements one might mention the following: improved phosphorus production by heating powdered bone ash with sand; use of metal oxides (of iron, chromium and copper) as contact bodies in the catalytic manufacture of fuming sulfuric acid (1852); production of calcium carbide ( $\text{CaC}_2$ ) to obtain acetylene (1862) which plays now an important



part in chemical industry. Calcium carbide itself is used to produce lime nitrogen ( $\text{CaCN}_2$ , calcium cyanamide), a most widely used and useful artificial manure. The method was developed in 1896 by Adolf Frank (1834-1916), a big industrialist who started the potassium industry, and Nicodem Caro, a Berlin industrial chemist. Woehler also analyzed many minerals, meteorites, etc., and made special investigations of antimony, boron, cerium, palladium, thallium, silicon, etc.

Of Woehler's work in organic chemistry the following additional achievements should be noted: quinone and quinoid compounds (hydroquinone, quinohydrine) and work on alkaloids (cocaine, narcotine, etc.). Also, working at high temperatures under pressure (in the bomb tube), he developed a method from which the synthetic production in autoclaves grew, as well as the reduction of organic compounds by heating with arsenous acid. These and other methods developed by him found wide industrial use.

As an academic teacher Woehler acted at Goettingen in a manner similar to that of Liebig at Giessen. His laboratory was extended several times and became a model for other university laboratories. Woehler was also a prolific writer. He wrote an "Outline of Chemistry" that appeared in two parts: "Inorganic chemistry" in 1831 and "Organic chemistry" in 1840. They were re-issued a number of times and translated into Danish and Swedish. In 1849 he published "Examples for training in analytical chemistry," called in later editions "Mineral analysis in examples." He wrote the "Pocket dictionary of pure and applied chemistry" with Liebig and the Berlin professor Johann Christian Poggendorff (1796-1877) and published from 1838, with Liebig, the "Annals of Chemistry and Pharmacy." He made a valuable translation of the writings of his Swedish teacher Berzelius; he was also responsible for the German publication of Ber-

zelius' "Manual of Chemistry" and his regular "Annual reports."

The third great German chemist of that time was Robert Wilhelm Bunsen (1811-1899).

He was born at Goettingen on March 30, 1811, the son of a university professor and librarian whose father and grandfather had worked in the mint. Bunsen went to school at Goettingen and Holzminden and then at the university of his home town studied chemistry (under Stromeyer), physics, mineralogy, geology and other natural sciences. He got his Ph.D. at 20. For a year and a half in 1832-3 he made a study trip that took him to Germany (as far as Berlin), Switzerland, the Tyrol, France (with a long stay in Paris) and Austria (as far as Vienna). He travelled long parts of the way on foot, visited many industrial enterprises and established personal contacts with a number of important people. He became a chemistry lecturer at Goettingen and, after his teacher Stromeyer died on August 18, 1835, he took over provisionally his chair and laboratory. When Woehler was called to Goettingen in the spring of 1836 he took over his Cassel post. While working with Cadet's fuming liquid on November 9, 1836 he damaged his right eye seriously in an explosion, which did not prevent him from completing his very laborious and dangerous task. He did no further work in organic chemistry; his attention was from then on concentrated on processes that can be followed with weight, number and measure. He was one of the chief founders of physical chemistry. He was called to Marburg University in the fall of 1839 and took part in 1846 in a geological expedition to Iceland organized by the Danish government. After three semesters at Breslau he finally accepted in the fall of 1852 a call to Heidelberg and remained one of the glories of its university until his death on August 16, 1899. Heidelberg erected a monument for him in 1908,

and his name has been honored by the German Bunsen Society for Applied Physical Chemistry.

Bunsen's work is almost entirely confined to inorganic and physical chemistry. After observing the precipitation effect of iron hydrate on solute arsenous acid he started in 1834 a series of physiological experiments with the Goettingen physician Arnold Adolf Berthold (1803-1861). They resulted in the discovery that iron hydrate was an effective antidote in arsenic poisonings. Cadet's fuming liquid, discovered in 1760 by the French chemist Cadet de Gassicourt (1731-1799) by heating a mixture of white arsenic and potassium acetate and also called "pyrophor" because of its capacity for self-inflammation, has some very strange qualities which made young Bunsen engage in a five years' investigation (1836-1841), a job that frightened away other chemists. He proved that the liquid contained a very complex organic compound of arsenic (alcarsin) whose properties and behavior towards other chemical substances he carefully investigated. This complex  $(CH_3)_2As-$ , called "cacodyl" by Berzelius because of its evil smell, could be, like a unitary element, converted unchanged from one compound to another. Together with Liebig's and Woehler's benzene, the new radical became an important argument in favor of the radical theory.

Bunsen's work in inorganic theory culminated in his investigation of the samples of minerals, liquids and gases that he brought back from Iceland. He not only improved the silicate analysis in his attempts to establish the exact composition of the minerals. He also tried to establish the mode of formation of the various types of mineral through bulge analysis and thus introduced the genetical concept into geology. He developed a new theory to account for the periodic phenomenon of the Icelandic hot springs.

In investigating the processes in iron and copper foun-

dries he was led to gas analysis for which he largely created the methods and apparatus. The foundry industry greatly benefited from this, first in Germany and England, then the world over. In 1857 he analyzed the combustion products of gunpowder with his Russian pupil Leon Shishkov (1830-1908), who later taught at the artillery school at Saint Petersburg. They cleared up the chemical processes occurring in the explosion.

Bunsen helped the development of volumetric analysis by working out the new method of iodometry that proved exceedingly useful for the determination of very small quantities.

Bunsen constructed in 1855 the burner that bears his name. A lateral supply of air secures total combustion of the lighting gas used. It proved of immense value to experimental physics and chemistry, to technology and to households. It also helped his pupil Auer von Welsbach to invent the incandescent gas light later on. Bunsen used the burner to work out in 1859 a new and basic analytical method, the spectrum analysis, together with Gustav Kirchhoff (1824-1887) whom he had specially called in from Breslau and who later became professor in Berlin. Spectrum analysis not only made it possible to trace very small quantities of elements that are untraceable by ordinary analysis, which led to the discovery of new elements and to the working out of "trace analysis." It also became possible to do something hitherto held to be impossible: to determine the chemical composition of the sun and of the fixed stars through spectroscopic observation.

Together with his English pupil Henry Roscoe (1833-1915, later professor at Manchester) Bunsen performed photochemical investigations on the effects of light on a mixture of chlorine and hydrogen (detonating gas) in 1855-62. Oswald called it "Bunsen's experimental masterpiece"

because of the great difficulties that had to be overcome. The mysterious phenomenon of "photochemical induction" observed in this connection was cleared up only half a century later by the two Manchester scientists C. H. Burgess and D. L. Chapman and proved to be the effect of very small gaseous impurities (ammonia, etc.).

Science owes to Bunsen some other important apparatus in addition to the Bunsen burner. The galvanic battery produced in 1839 by Sir William Grove (1831-1896), who started as a jurist and ended as physics professor in London, consisted of zinc in diluted sulfuric acid and platinum in concentrated nitric acid. Bunsen replaced the expensive platinum by cheap coal (a mixture prepared from coal and coke). The Bunsen battery permitted the relatively inexpensive production of strong electric currents and dominated the strong-current techniques until replaced by Siemens' dynamo. Bunsen himself used it to obtain by electrolysis magnesium (1852), chromium, strontium and other metals, especially aluminum (1854) which later led to large scale industrial production.

Bunsen's French friend Jules Reiset published in 1842 in an article on the zinc-coal battery the description of a very simple photometer. Bunsen simplified it still further by replacing a smaller paper disc glued to a larger paper disc by a fat spot.

To determine the density of gases Bunsen used narrow nozzles to measure discharge velocity under a certain pressure. He improved in 1870 the ice calorimeter by using the volume decrease of ice in melting for measuring. Towards the end of his scientific career, in 1887, he constructed a special steam calorimeter. One of his most widely used inventions was the water jet air pump of 1868. One might finally mention the Bunsen valve, consisting of a slit in a rubber tube.

Spectrum analysis led to the discovery of several elements. Bunsen himself found caesium in 1860 in the Durckheim brine and rubidium in 1861 in a Saxon lepidolith. In the same year thallium was discovered in London by William Crookes from selenium mud of the Tolkerode sulfur plant in the Harz mountains. Ferdinand Reich (1799-1882), physics professor at Freiberg, and Theodor Richter (1824-1898), professor and director at the Freiberg mining academy, discovered indium in 1863 in the Freiberg zinc blende. The Paris astronomer Pierre Jules Cesar Janssen (1824-1907) noted in observing an eclipse of the sun in India in 1868 in a protuberance of the sun's chromosphere the light yellow line of an unknown element. Lockyer and Frankland called it "helium," from the Greek helios, sun. The Italian physicist Luigi Palmieri (1807-1896) found it in 1895 in the Vesuvius lava and William Ramsey and Th. Cleve also in 1895 in the pitchblende cleveite. Gallium was discovered in 1875 by Lecoq de Boisbaudran in a zinc blende from the Pyrenees, and scandium in 1879 by Lars Fredrik Nilson (1840-1899), professor at Upsala, in gadolinite, also by spectrum analysis. Rare gases and other new elements were discovered in the same way.

The development of chemistry in the 19th century is so rich and the number of the scientists involved so large that a brief survey such as this cannot give detailed personal data. Only the most important achievements in the various areas of chemistry can be given here and lead up to the state of chemistry today.

## VI. DEVELOPMENT OF VARIOUS BRANCHES OF CHEMISTRY TILL THE BEGINNING OF THE 20TH CENTURY.

### 1. *Theoretical organic chemistry*

After some attempts, not unsuccessful, by men like Glauber and Scheele, a systematic investigation in the field of organic chemistry became possible only after ultimate analysis reached the stage when it could easily give the percentage composition of organic compounds consisting of some few elements (C, H, O, N). Georg Ludwig Carius (1829-1875), a pupil of Bunsen who taught at Marburg, developed in 1860, a simple procedure to determine halogens, sulfur and phosphorus in organic compounds: heating with concentrated nitric acid in bomb tube or, in the case of halogens, with silver nitrate.

Scheele had already proved that there were, in addition to the familiar acetic acid, other organic acids in nature. He also proved the existence of glycerin in fats but did not explain its connection with the different fatty acids. The composition of fats and oils was made clear by the detailed researches of Michel Eugene Chevreul (1786-1889), a color chemist who was professor in Paris and was known because of his age—he died at 103—as “the Nestor of chemistry.” He published his results in 1823 under the title of “Chemical researches on fatty matters.” This led by 1825 to the manufacture of stearine candles, consisting of free fatty acids,

which represented a considerable progress in lighting over the old smoldering tallow candles.

Scheele, too, had already carried out an organic synthesis from inorganic substances by producing potassium cyanide from graphite, potash and sal ammoniac. Only half a century later Woebler managed the artificial production of oxalic acid and urea which is generally considered the first organic synthesis. Berzelius, who was very much surprised to find the law of chemical proportions valid also in organic chemistry, tried to create some order in the jungle of organic compounds with his radical theory. Radicals containing oxygen, e.g. benzoyl, could, in accordance with his dualistic hypothesis, be viewed only as oxides and hydrates of the genuine radicals, consisting only of carbon and hydrogen. Liebig placed ethyl ( $C_2H_5$ ) beside benzyl ( $C_6H_5$ ) and considered alcohol to be the hydrate and ether to be the oxide of that radical. Dumas and Boullay in 1828 regarded ether as the hydrate of an "etherine" radical ( $C_2H_4$ ). This view had to be abandoned when Zeise discovered the mercaptans in 1834. The radical theory reached its climax with Bunsen's acetyl investigations of 1837. The radicals were the "organic elements" and Liebig described organic chemistry as "the chemistry of composite radicals."

The hypothesis of unchangeable radicals could not be upheld when the replaceability of hydrogen by chlorine was demonstrated in 1834 by Jean Baptiste Dumas (1800-1884), a chemistry professor in Paris who dabbled in politics and served as minister in 1848. Dumas was an excellent experimentalist and a good writer; his methods to determine vapor density and nitrogen are particularly important. He also showed that the hydrogen atom could be generally replaced by a halogen or half an oxygen atom. Dumas called this phenomenon "metalepsy" (from the Greek *metalepsia*, exchange); it was later re-named "substitution." Chloro-



acetic acid proved to be not substantially different from the original acetic acid. And so Berzelius' dipolar dualistic view had to yield in organic chemistry to a unitary view. The substitution theory was both a contribution to the clarification of the general equivalency concept and the first beginning of the valency theory developed later. Dumas called "types" the various atomic groups that remain substantially unchanged in character when hydrogen is exchanged for other elements; his theory is therefore known as "the older type theory." His countryman Auguste Laurent (1807-1853), professor of chemistry at Bordeaux who became the head of the Paris mint in 1848, developed in 1836 the nuclei theory by distinguishing between "original nuclei" (the actual radicals) and "derived nuclei" (radicals altered by substitution). Laurent also set up in 1845 the law of even atomic numbers: the number of hydrogen atoms in a nitrogen-free compound must be even and in a nitrogen-containing compound it must be odd.

His friend and collaborator Charles Gerhardt (1816-1856), a pupil of Liebig who taught at Montpellier, Paris and Strasbourg, called the components of chemical compounds which unite in mutual interaction with the freeing of atomic "residues," which cannot exist by themselves. His residues theory was a combination of the radical and substitution theories.

The theoretical structure not only of organic chemistry but of chemistry generally required clarification. There reigned a great confusion in the 1840's about the basic concepts of atom, molecule, equivalence, etc. The clarification was achieved by organic chemists, especially Laurent. He defined, in accordance with Avogadro's hypothesis, the molecular weight of an element or a compound as the weight which in gaseous state and under the same conditions occupies the same volume as two weight parts (one double

atom or one molecule) of hydrogen. A molecule is, according to Laurent, the smallest quantity required to form a chemical compound; the atom the smallest quantity of an element that appears in chemical compounds. An equivalent is "the equivalent quantity of analogous substances." If an element combines with others in different weight proportions, then it has various equivalents or valencies.

Gay-Lussac developed in 1811 a steam density measuring procedure for experimental determinations of molecular weights. Weighed quantities of solid or liquid bodies are vaporized and the volume occupied by the vapor is determined. Dumas proceeded on an opposite path in 1827: he vaporized any quantity of a solid or liquid substance in a narrow-necked flask whose volume was known and determined the weight of the vaporized quantity after fusing the neck. A. W. Hofmann improved in 1868 Gay-Lussac's method by using longer measuring tubes and adding a steam jacket. Finally, in 1873 Victor Meyer added a very practical device: instead of measuring the volume of the vapor he measured that of the quantity of air it displaced.

The man most responsible for the final theoretical clarification of atoms, molecules, etc., was Stanislao Cannizzaro (1826-1910), professor at Genoa, Palermo and Rome, who is also known for his valuable work in organic chemistry, e.g., the Cannizzaro reaction in the conversion of aldehyde into alcohol and acid. Cannizzaro's 1858 pamphlet, "Epitome of a course in philosophical chemistry," was distributed to the participants of the international chemistry congress at Karlsruhe in 1860.

The Alsatian Adolph Wurtz (1817-1884) achieved much for organic and general chemistry. He was a pupil of Liebig and Dumas and taught in Paris. He managed to obtain alkyl amines by the action of caustic potash on cyanic acid esters. The man who managed to obtain such compounds syn-

thetically from ammonia and halogen alkyls was August Wilhelm Hofmann (1818-1892), a pupil of Liebig. After a long and successful career at the London Royal College of Chemistry he became professor at Bonn in 1864 and in Berlin in 1865. He founded the German Chemical Society in 1865 and was ennobled. He was equally important as teacher and investigator. The new nitrogen-containing compounds were put together as "ammonia type," to which "water type" compounds were added. Laurent replaced the  $H_2O$  formula of water by  $HO$  in 1846 and described alcohol and ether as its derivatives. Alexander William Williamson (1824-1900), a pupil of Liebig who taught in London, proved in 1850 that this view was correct by producing mixed ethers.

Gerhardt outlined on the basis of these results a new theory of four types: hydrogen ( $H-H$ ); hydrogen-halogen ( $H-Cl$ ); water ( $H-O-H$ ) and ammonia ( $NH_3$ ). By replacing individual hydrogen atoms with radicals or groups of atoms it is possible to derive all kinds of chemical compounds from these four types. The schematic possibilities were increased by the doubling of types and by their combinations into "mixed types" and a "unitary system" could thus be set up. Gerhardt created the concept of "homologous series" on the basis of an observation made in 1842 by Jacob Schiel (born 1813), who taught at Heidelberg and lived in America, that hydrocarbons differ from each other by having more or less of one or many  $CH_2$ -groups. Hermann Kopp (1817-1892), professor at Giessen and from 1863 at Heidelberg who specialized in industrial as well as physical chemistry, was responsible for further progress in this direction. He worked on the gradual changes in physical qualities like boiling points, molecular volumes, etc., occurring with changing  $CH_2$  content.

The type theory had to be constantly adjusted to take

care of new compounds. "Subsidiary" types had to be created in addition to double and mixed types, e.g., the  $\text{H}_2\text{S}$  of mercaptans in addition to  $\text{H}_2\text{O}$ .

Hermann Kolbe (1818-1884) turned against this overweening formal schematism. He was born at Elliehausen near Goettingen as the son of a village minister. He studied under Woehler and Bunsen and in 1845/7 in London under L. Playfair, then returned to Marburg with E. Frankland. He spent some years as a writer at Vieweg in Brunswick. In 1851 he became Bunsen's successor at Marburg and was professor at Leipzig from 1865 till his death. From 1869 onwards he edited the "Journal for practical chemistry" founded by O. L. Erdmann (1804-1869). Kolbe was, like Liebig, a bonny fighter. His dissertation, started at Goettingen and completed at Marburg (1842-3) contained important results. By the action of chlorine on carbon disulfide he obtained, in addition to other chlorine compounds, a crystalline substance, which had also been obtained in 1813 by Berzelius and A. Marcet (1770-1822). By treating it with a caustic potash solution, Kolbe was able to convert it into the potassium salt of trichloromethane sulfonic acid. Kolbe called it chlorocarbonic hyposulfuric acid and, in accordance with Berzelius' view, considered it a "paired compound" of trichloromethyl and hyposulfuric acid. By the action of sodium amalgam he was able to replace the chlorine atoms by hydrogen, one after the other, and thus obtain the chlorine-free methyl hyposulfuric acid. Similarly, Louis Melsens (1814-1886) succeeded shortly before in converting trichloroacetic acid, which had been called trichlorocarbonic oxalic acid as a "paired compound," into acetic acid. When Kolbe obtained, in addition to perchloroethane, trichloroacetic acid by the action of moist chlorine in sunlight on "simple carbon chloride" ( $\text{C}_2\text{Cl}_4$ ), which he produced passing carbon tetrachloride through an incandescent tube, the necessary pre-

conditions for the artificial production of acetic acid were attained. Kolbe wrote in 1845:

"The interesting fact results that acetic acid, hitherto known only as the oxidation product of organic matter, can now be also directly composed by a synthesis of its elements. If it were possible to convert acetic acid into alcohol and obtain sugar and amyl from the latter, we would be obviously able to compose these general components of the vegetable kingdom artificially from their remotest components."

Kolbe uses here the word "synthesis" as meaning the artificial production of organic compounds. He prophetically forecasts the growth of synthetic chemistry from its modest beginnings to its present great achievements.

Hermann von Fehling showed how benzonitril ( $C_6H_5CN$ ), obtained by heating benzoate of ammonium, could be converted into benzoic acid by the action of both acid and alkali. Kolbe and Edward Frankland (1825-1899, later professor at Manchester and London) tried to apply this procedure to ethyl and methyl cyanides obtained by Theophile Jules Pelouze (1807-1867, a pharmacist who later taught at Lille and Paris and an important analytical chemist who was specialist in atomic weights), as well as by Dumas and Peligot. They thus obtained propionic and acetic acid by "saponification," as it was later called. This opened up a new method of synthesis of organic acids, also polybasic, which were conceived as paired compounds of oxalic acid with corresponding alcohol residues. In attempting to decompose these paired compounds into their components by the action of an electric current, Kolbe obtained from acetic acid, in addition to carbon dioxide, a gas which he held to be free methyl but which proved to have double molecular quantity (ethane,  $C_2H_6$ ). Frankland tried in vain to obtain the free ethyl radical by the action of zinc on ethyl

iodide. Instead he obtained in 1856 zinc ethyl and was thus persuaded that alcoholic residues are unable to exist in a free state. From the point of view of the pairing theory Bunsen's cacodyl was also viewed as a paired compound of arsenic and methyl, corresponding to the composition of the radical of acetic acid called by Berzelius "acetyl" ( $\text{CH}_3\text{CO}-$ ), in which methyl was assumed to be paired with carbon ( $\text{CH}_3\text{C}$ ).

Frankland's thorough investigation of organic compounds with nitrogen, arsenic, antimony, phosphorus, etc., in 1853 proved that these elements combine with either three or five univalent groups. The concept of "valence" was directly connected with the nature of the regularity of simple and multiple proportions found in investigating inorganic compounds. But it was finally clarified only gradually in connection with the much more difficult organic compounds. Frankland's work on metal-organic compounds was helpful in this respect. Each element thus had to be attributed a valence or "saturation capacity": but this could appear in different magnitudes in the same element.

These results influenced Kolbe's views on the composition of organic acids. As he generally tried to derive organic compounds from the inorganic, he assumed that carbon dioxide, which plays a basic part in nature for the biological growth of plants, was the prototype of organic acids. Carbonic acids, aldehydes, ketones, alcohols and finally hydrocarbons are created when the oxygen valences of carbonic acid  $(\text{C}_2\text{O}_2)\text{O}_2$  or its hydrate  $(\text{C}_2\text{O}_2)(\text{OHO})_2$  are replaced one after the other by hydrogen or alkyl residues. Polybasic acids and polyacidic alcohols can be derived similarly from two or more molecules of carbonic acids. Likewise, the sulfonic acids, sulfones, phosphorus, arsenic and other compounds can be derived from the correspondent inorganic compounds.

Kolbe contrasted these "real types" with Gerhardt's "formal types" which he rejected as unscientific playing with formulas. Kolbe was so sure he was right that he could in 1859 foresee the existence of hitherto unknown compounds like secondary and tertiary alcohols. These were, indeed, discovered in 1862 by Charles Friedel (1832-1898), professor in Paris, and in 1864 by Alexander Butlerov (1828-1886), professor at Kazan and Saint Petersburg. There was a similar experimental confirmation for the isomeric phenomena in the series of fatty acids that Kolbe had theoretically deduced. The composition of oxy- and aminoacids, that had baffled several other scientists, was also cleared up. Kolbe managed in 1859 to synthesize salicylic acid by the action of carbonic acid on phenol in the presence of sodium. He improved this method when he resumed his experiments by treating sodium phenolate with  $\text{CO}_2$  in heat. In 1874 a factory for the artificial production of salicylic acid could be started by Heyden in Dresden-Radebeul.

The task of organic synthesis fully occupied the great French chemist P. E. Marcellin Berthelot (1827-1907), professor at the College of France, Minister of Education in 1886-7 and of Foreign Affairs in 1895-6. He tried to obtain, among others, formic acid, acetylene and benzene from elements or inorganic matters. He was also an active writer: in 1860 he published his book "Organic chemistry based on synthesis." Later on he devoted himself to thermochemical problems and proclaimed in 1867 the "third principle": each chemical conversion proceeds in such a way that the greatest quantity of heat is developed in the process. In 1879 appeared his "Chemical mechanics based on thermochemistry." He also made valuable researches into the history of alchemy.

August Kekulé von Stradonitz (1829-1896) made especially valuable contributions to the clarification of constitu-

tion. He was a pupil of Liebig. After a long stay in Paris, Switzerland and London he became lecturer at Heidelberg in 1856. From 1858 through 1865 he was professor at Ghent and from 1865 till his death in Berlin. He was "the philosopher of chemistry." While Kolbe had some concepts of the valence or, as it was then called, the "atomicity" of carbon, it was Kekulé who clearly expressed them in 1858. The word "valence" was later proposed for the validity or atomicity by Carl Hermann Wichelhaus, Berlin professor of chemical technology who introduced the alkali melting of sulfonic acids into industry. In 1857 he proclaimed carbon to be quadrivalent. He also accepted the theory of auto-concatenation of the carbon atoms proposed in 1852 by Friedrich Rochleder (1819-1874), a phytochemist who was chemistry professor at Lemberg, Prague and Vienna. For a time he believed in changeable valence but he finally held that the quadrivalence of carbon was as unalterable as its atomic weight. He added the simplest carbon compound, methane ( $\text{CH}_4$ ) as fifth type to Gerhardt's four types. All organic compounds can be derived from this prototype by gradual exchange of its four hydrogen atoms for other atomic groups or elements.

The idea of auto-concatenation of carbon atoms was simultaneously proclaimed by the Scot Archibald Couper (1831-1892), Playfair's assistant at Edinburgh. Couper clearly recognized its importance for the further growth of organic chemistry but he believed in changeable valence. Couper also originated the valence dashes with which Kekulé wrote his constitutional formulas and thus became the founder of structural chemistry. Young Couper had a nervous breakdown in 1858, shortly after the appearance of his two fundamental papers, and did nothing more for science from then on. The robust Kekulé, who stated that the idea of atomic concatenation and thus the founding of structural chemistry



came to him in a dream image during a night trip through London in a bus, started in 1859 a "Manual of organic chemistry" in several volumes, but could not finish it. His pupil and successor Richard Anschuetz (1852-1919), professor at Bonn, also continued it but could not finish it.

Among other scientists who helped to develop structural chemistry one should mention: Butlerov who coined the name "structure"; Heinrich Ludwig Buff (1828-1872), professor at the Prague German Polytechnic; Emil Erlenmayer (1825-1909), professor at Heidelberg and the Munich Technical Institute, and Joseph Loschmidt (1821-1895), physics professor in Vienna.

The so-called unsaturated compounds or olefines played a special part in clearing up the question of carbon valence. Unlike the paraffins, the carbon does not seem to be linked with other atoms in all its valences. Various scientists vainly tried to obtain methylene ( $\text{CH}_2$ ), the lowest link of unsaturated hydrocarbons that would correspond to carbon dioxide. Only the next lowest link, ethylene ( $\text{C}_2\text{H}_4$ ) could be obtained. To maintain the quadrivalence of carbon, Loschmidt introduced the concept of double linkage of carbon atoms which he expressed by the double hyphen ( $\text{H}_2\text{C}=\text{CH}_2$ ); in acetylene he assumed a triple linkage ( $\text{HC}\equiv\text{CH}$ ). The resulting contradiction, that multiple linkages were looser than simple ones, remained unclarified for a time. Loschmidt was the first to try to express the spatial arrangement of interrelated atoms in formulas and thus to present certain isomeric phenomena pictorially. A. W. Hofmann proposed the generally accepted endings "ane," "ene" and "ine" to describe the saturated and unsaturated hydrocarbons.

Benzene ( $\text{C}_6\text{H}_6$ ), discovered by Faraday in 1825 and closely investigated by Mitscherlich, the basic substance of the so-called aromatic compounds, offered special difficulties

in the way of adequate formulas. It is unsaturated according to its formula; but it behaves in a fully saturated manner, different from that of paraffins. The synthesis of toluol was achieved in 1864 by the action of sodium on a mixture of benzene bromide and methyl iodide by Rudolf Fittig (1835-1910), a pupil of Woehler who taught at Tuebingen and Strasbourg, and his pupil Bernhard Tollens (1841-1918), professor of agricultural chemistry at Goettingen from 1873. But with ethyl iodide they did not obtain the expected xylol but the different compound ethyl benzene. Kekulé was thus inspired in 1865 to posit a benzene formula in which six carbon atoms with alternately simple and double linkage are united in the shape of a ring so that every carbon atom keeps a free linkage for hydrogen. Kekulé also dreamed up this formula, this time in front of a fireplace at Ghent. Since there exist no two isomeric orthoderivatives of benzene, Kekulé replaced in 1872 the alternative simple and double linkage by an oscillatory state of carbon compounds. Loschmidt had already in 1861 proposed in a fairly obscure publication "Chemical Studies" that benzene had a six-atom carbon nucleus which he pictorially presented as a circle with six<sup>\*</sup> attachment points. But he did not explain the isomerism of the three cresols.

Other benzene formulas were proposed. Adolf Claus (1840-1900), a pupil of Kolbe and Woehler who taught at Freiburg, tried to overcome the difficulty of the alternately single and double linkage by uniting diagonally the atoms located opposite each other in the hexagonal ring (1867). Wilhelm Koerner, a pupil of Kekulé and Cannizzaro who taught at Milan, also developed a diagonal formula. He solved the problem of "location determination" in 1866-74 by clearing up the position of the lateral groups in the benzene nucleus—ortho-, meta-, parasymmetric, asymmetric and vicinal. Albert Ladenburg, a pupil of Kekulé and

Wuertz who taught at Kiel and Breslau, and who in 1869 proved the equivalence of six hydrogen atoms in the benzene nucleus, proposed in the same year a prismatic formula: two triangular CH-rings linked by three single bonds. Lothar Meyer (1830-1895), originally a physician who was a pupil of Loewig and Bunsen and taught at Eberswalde, Karlsruhe and Tuebingen, proposed a different interpretation. He assumed (1865, 1872) a centric saturation of the six free carbon valencies. This idea was accepted in 1887 by Henry Armstrong (1848-1899), a pupil of Kolbe who taught in London, and in 1888 by Adolf von Baeyer (1835-1917), a pupil of Bunsen and Kekulé, who became professor at Strasbourg in 1873 and at Munich in 1875 and was awarded the Nobel prize in 1905. The four most important benzene formulas are:

- Hexagonal ring: Kekulé (1865)
- Diagonal formula: Claus (1867)
- Koerner (1874)
- Prismatic formula: Ladenburg (1869)
- Centric formula: L. Meyer (1865)
- H. Armstrong (1887)
- A. v. Baeyer (1888)

Of these, Kekulé's benzene ring became more and more accepted. It was so important for the large chemical industry that it honored Kekulé in 1890 on the occasion of the 25th anniversary of his formula.

Kekulé set up other hypotheses. He thought he could interpret certain isomerisms as looser and denser linkages of atoms. He assumed, for double linkages, a number of atomic swings or pushes double that for single ones. He also assumed that the four valencies of the carbon atom were directed towards the four corners of a tetrahedron, an as-

sumption made already in 1808 by the brilliant Englishman W. H. Wollaston. It was thus possible to represent the pattern of a double and even a triple linkage. But Kekulé did not pursue the idea to its last logical consequences for the spatial arrangement of atoms. Louis Pasteur (1822-1895), professor at Strasbourg and Paris who became especially famous for his cure of rabies, made some beginnings in this direction. In 1848, on the basis of his crystallographic investigations of the salts of dextro- and levotartaric acids, he stated that the asymmetry of crystal formations was due to an asymmetric construction of molecules.

Structural chemistry made it possible to set up satisfactory formulas for most organic compounds. But further research revealed cases of isomerism that could not be explained by different structural formulas. Johannes Wislicenus (1835-1905), a pupil of Horsford at Cambridge, Mass., and of W. Heintz at Halle, who taught at Zurich, Wuerzburg and Leipzig, concluded in 1873 from his investigation of the sarcolactic and fermentation lactic acids that "the difference can be based only on the different spatial arrangement of the atoms linked to each other in the same sequence." Sarcolactic acid, unlike fermentation lactic, proved optically active: it rotates the plane of polarized light to the right. The solution of this difficult task which carried structural chemistry from the two-dimensional plane of paper into three-dimensional space was due to two young scientists, aged at the time 27 and 22. They were Jules Achille Le Bel, a pupil of Wurtz who later lived as a man of wealth in Paris, and Jacobus Henricus van't Hoff (1852-1911).

a pupil of Kekulé and Wurtz who taught at Amsterdam from 1878 and at the Berlin Academy of Sciences from 1896 and who was awarded the Nobel prize in 1901. To explain the phenomenon called by Wislicenus "geometric isomery" they came out in 1874 simultaneously but inde-

pendently with a theory in which the idea of a carbon tetrahedron, already outlined by Wollaston and Kekulé was developed to its last consequences into a spatial structural chemistry. Optical activity was explained by an "asymmetric carbon atom" which binds four different atom groups at its four valencies directed into space. Adolf von Baeyer developed in 1835 a "theory of valency tensions" for the ring-closure on the basis of his work on hydrogenated benzene derivatives. He introduced in 1838 the terms "cis" and "trans" configurations for the isometry of saturated and unsaturated compounds of, e.g., maleic and fumaric acid. Victor Meyer (1848-1897), a pupil of Bunsen and Baeyer who became professor at Stuttgart in 1871, at Zurich in 1872, at Goettingen in 1885 and at Heidelberg in 1889, described in 1888 the "constitution taking into account the geometrical position" as "stereochemical constitution"—hence the name "stereochemistry." Meyer also created the name "desmotropy" for the phenomenon of bond exchange between individual atoms, e.g. oxygen in keto- and hydroxyl linkage. Conrad Laar, who taught at Bonn, called it "tautometry" in 1885. Julius Wilhelm Bruehl (1850-1911), a pupil of Hofmann and Landolt who was professor at Lemberg and honorary professor at Heidelberg from 1887, made detailed spectroscopic investigations to determine the relation of refractivity to intramolecular linkages and to clear up the chemical properties of organic compounds.

A number of scientists did useful work for preparative and synthetic organic chemistry. They were—Adolf Wuertz: conversion of cyanogen compounds into alkylamines: preparation of polyvalent alcohols: synthesis of mixed radicals from halogen alkyls by the action of alkali metal. Rudolf Fittig: synthesis of aromatic-aliphatic compounds from their halogen compounds by the action of alkali metal—the "Fit-

tion synthesis" of 1864. Charles Friedel and James Crafts (1839-1917), a professor at Boston who often stayed in Paris: synthesis of aromatic-aliphatic compounds from benzene (or derivatives) in the presence of aluminum chloride—the Friedel-Crafts reaction of 1877. Carl Schotten (1853-1910) of the Berlin Patent Office and Eugen Baumann (1846-1896), the Freiburg professor who discovered thiodiodine: synthesis of esters and acid amides by the action of acid chlorides (e.g., benzoyl chloride), the Schotten-Baumann reaction of 1884. Traugott Sandmeyer (1854-1922), a pupil of Victor Meyer who was a chemical engineer at Basel: replacement of the azo group by halogen, cyanogen, hydroxyl, hydrogen—the Sandmeyer reaction of 1884. Paul Sabatier, professor at Toulouse awarded the Nobel Prize in 1912. and Jean Baptiste Senderens, professor at Toulouse: hydrogenation of organic compounds by the catalytic action of nickel and other metals in 1897, a method very successfully applied to chemical industry since 1902 by Wilhelm Normann,

a chemical engineer: hardening of fats: reduction of  $\text{CO}_2$  to aldehydes, alcohols, hydrocarbons. Victor Grignard professor at Nancy and Lyon awarded the chemistry Nobel prize in 1912: syntheses by the action of organic magnesium compounds on aldehydes, ketones, etc.—the Grignard reaction of 1900-1.

Kekulé could not maintain for long his rigid view of the unalterable quadrivalency of carbon. Johannes Thiele (1865-1918), a pupil of Baeyer who taught at Munich and Strasbourg, assumed in 1899 that the valency was divisible. Paul von Walden, professor at Odessa, Riga, Saint Petersburg, Rostock, Frankfurt and Tuebingen and a historian of chemistry, made an interesting observation in 1896: when one substituent of an asymmetric carbon atom is replaced by another it is possible in certain cases to re-

verse the rotation direction of polarized light it became known that organisms use this "Walden inversion" to convert the unnatural right-turn amino acids into left-turn forms.

After the constitution of fats had been cleared up by Chevreul two of the three great groups of natural foods still remained to be investigated: the hydrocarbons and the albuminous substances. A number of chemists undertook this task, first with regard to the carbohydrates (starch, sugar, cellulose). The first man to attempt the synthesis of sugar was Butlerov. In 1861 he obtained a sugar mixture, "methylenitane," by the action of milk of lime on trioxymethylene. A quarter of a century later the work was resumed by Oskar Loew, a Munich professor who spent many years in Japan and who developed in 1886 with B. Tollens a simple method for the catalytic production of formaldehyde ( $\text{CH}_2\text{O}$ ) from methyl alcohol: vapors are passed over incandescent copper spirals; the resulting 20% to 30% mixture is called formalin. He obtained from formaldehyde by the action of milk of lime another sugar mixture he called "formose." Later, in 1889, he obtained by the action of magnesia maltose, which could be fermented. Other investigators of hydrocarbons were Bernhard Tollens and Heinrich Kiliani, professor at Munich and Freiburg.

But full clarification was obtained only by the studies, started in 1884, of Emil Fischer (1852-1919), a pupil of Baeyer who taught at Erlangen, Wuerzburg and Berlin and was awarded the 1902 Nobel chemistry prize. The phenylhydrazine he developed in 1875 proved a very valuable aid (formation of "osazones" and "osones"). Together with Julius Tafel (1862-1918), later professor at Wuerzburg, he succeeded in 1890, starting from glycerin (acrolein, etc.), in synthesizing a number of natural sugars (-acrose i-fruc-

tose, manose, glycose, etc.). The sugars were recognized as polybasic alcohols with an aldehyde or keto group (aldoses and ketoses) which were either monomolecular (hexoses,  $C_6H_{12}O_6$ , pentoses, tetroses) or are linked with each other in the manner of ethers as "bioses" (e.g., cane sugar,  $C_{12}H_{22}O_{11}$ ). Fischer also produced new artificial sugars and clarified the stereochemistry of the sugar molecules and the close relationship between the spatial molecular configuration and specific ferment (like key and lock). The old controversy between Liebig and Pasteur on the nature of the fermentation of sugar was solved by Eduard Buchner (1860-1917), who taught at Wuerzburg and Berlin and obtained the 1907 Nobel chemistry prize. His 1897 production of the yeast ferment "zymase" finally decided the issue against Pasteur.

Fischer also clarified the chemistry of albuminous substances by proving that their individual components were some two dozen different amino acids, linked to each other in the manner of carbamides. To these must be added groups containing sulfur and phosphorus. But it was not yet possible to attain a complete synthesis of natural albuminous compounds.

Fischer made especially thorough investigations of the compounds of the uric acid groups that had already interested Liebig and Woehler. Baeyer found in 1863-4 that these substances were carbamide-like compounds of urea and di-basic acids which he called "ureids." In 1875 Ludwig Medicus (1847-1915), professor at Wuerzburg, set up a formula of uric acids which proved correct. The first synthesis of uric acid was made by Johann Herbaczewski, professor at Prague, from urea and glycoll. More perfected and more important theoretically was the 1888 synthesis starting from urea and acetic ester (?) by Robert Behrend, professor at Hanover, and Oscar



Roosen. Fischer proved that the parent substance of "diureids" was purine ( $C_5H_4N_4$ ). The synthesis of the purine derivatives caffeine and theobromine was achieved in 1897.

The alkaloids were quite early scientifically investigated. The pioneer was Friedrich Sertürner (1783-1840), pharmacist at Paderborn, Einbeck and Hameln. As a 21-year-old pharmacy apprentice he proved that "somniferous principle" of poppy juice was not contained as was believed in a resin-like substance but that the effective component was a crystallizable basic substance which forms salts with acids. He published his results in 1805 and, after a thorough investigation, in 1817, Sertürner named the substance morphine after Morpheus, the Greek god of dreams. Wilhelm Meissner (1792-1853), a pharmacist at Halle, proposed in 1819 the name "alkaloids" for morphine and other effective vegetable substances discovered later because of their alkaline character as organic bases. However, a number of chemists had to labor hard to clarify their chemical constitution.

Wöhler was able to decompose in 1844 the alkaloid narcotine, also obtained from opium, into a component containing nitrogen (cotarnine) and one free from it (meconine). Cotarnine proved to be, as with other alkaloids, the really effective component. The Russian Ivan Vishnegradsky (1830-1895), professor at Saint Petersburg, and the German Wilhelm Koenigs (1851-1906), a pupil of Baeyer who taught at Munich, assumed that they were derivatives of pyridine and quinoline, an assumption that proved to be correct. Wilhelm Körner and J. Dewar developed in 1869-70 ring formulas, corresponding to benzene and naphthalene, for pyridine ( $C_5H_5N$ ), which was found in 1851 in bone oil and coal tar by Thomas Anderson (1819-1874), a pupil of Liebig who taught at Edinburgh and Glasgow, and also for quinoline ( $C_9H_7N$ ), discovered already in 1833 by F. F. Runge in coal tar and called "leukol" and obtained in 1842 by C. F.

Gerhardt by the decomposition of quinine. To these six-numbered "heterocyclic compounds" were added those with five-numbered rings: pyrrole ( $C_4H_5N$ ), discovered in 1833 by F. F. Runge in coal tar: furfurane or furane ( $C_4H_4O$ ), discovered as a carbon-oxygen ring by Heinrich Limpricht (1827-1909), a pupil of Woehler who taught at Greifswald; and thiophen, discovered in 1882 as carbon-sulfur ring in raw benzene by Victor Meyer.

#### Heterocyclic compounds:

Pyridine

Quinoline

Acridin

Pyrrole

Pyrazole

Glyoxaline  
(Imidazol)

Furane

Thiophen

Pyridine was obtained synthetically in 1877 by W. Ramsay from acetylene and hydrogen cyanide. Quinoline was obtained in 1879 by W. Koenigs (allyl aniline through incandescent tube) and in 1880 by Zdenko Hans Skraup (1850-1910), professor at Gratz and Vienna (aniline and glycerin heated with sulfuric acid). In 1836, Albert Ladenburg made the first synthesis of an alkaloid, conine. Fischer achieved in 1897 the synthesis of caffein and theobromin. Further synthesis followed in the 20th century.

Terpenes and camphor, belonging to the volatile oils, were

recognized as unsaturated compounds, standing between aromatic and aliphatic substances, and their constitution ( $C_{10}H_{16}$  and  $C_{10}H_{16}O$ ,  $C_{10}H_{18}O$ ) was gradually cleared up. Julius Bredt, a pupil of Fittig who taught at Aachen, developed in 1893 a "bridge formula" for camphor (a combination six-numbered and five-numbered ring) that has proved itself correct against other proposals. Among the important men in this area one might mention: Georg Wagner (1849-1903), professor at Warsaw; Philippe Barbier (1848-1922), professor at Lyon; Ossian Aschan professor at Helsinki, and Friedrich Wilhelm Semmler, professor at the Breslau technical institute.

The Nobel prize of 1910 was given to Otto Wallach, a pupil of Woehler who taught at Goettingen, for his excellent work on terpenes and camphor.

Using the hydroxylamine ( $NH_2OH$ ) obtained in 1865 by Wilhelm Lossen (1838-1906), professor at Heidelberg and Koenigsberg, by the reduction of nitric acid esters, Victor Meyer obtained in 1882 the so-called oximes (aldoximes  $RCH:NOH$ ; ketoximes  $R_2NOH$ ) by action on aldehydes and ketones. Heinrich Goldschmidt, professor at Oslo,

found in 1883 an isomeric benzil-dioxime ( $C_6H_5 \cdot C(NO) \cdot C(NO) \cdot C_6H_5$ ): and so Ernst Beckmann (1853-1923), a pupil of Kolbe who taught at Giessen, Erlangen and Leipzig and became in 1912 director of the Kaiser Wilhelm Chemistry Institute in Berlin, could obtain in 1887 a solid isomer from the liquid benz-aldoxime ( $C_6H_5 \cdot CH:NOH$ ) by action of concentrated sulfuric acid in the cold. The stereochemical views gained from the carbon atom were thus transferred to the nitrogen atom. Arthur Hantzsch, professor at Zurich, Wuerzburg and Leipzig, and Alfred Werner (1866-1919), professor at Zurich who won the Nobel chemistry prize in 1913, set up in 1890 the hypothesis that the three valencies of nitrogen were

directed radially. The nitrogen atom occupied a corner of a tetrahedron and the valencies follow the directions of the three angles issuing from it to the three other angles of the tetrahedron. Corresponding to the cis- and trans-forms of the double carbon bonds are syn- and anti-forms of double carbon-nitrogen bonds: syn-aldoxime, anti-aldoxime.

Werner made his stereometric views valid also for inorganic compounds and developed in 1893 his octahedron theory with the coordinate number 6 (for cobaltic compounds and other complex salts) by distinguishing between main and subsidiary valencies. Werner's coordination theory created a new system and nomenclature for complex compounds. His views received later a roentgenologic confirmation.

The stereochemical view proved right when applied to the curious transposition obtained in 1886 by Beckmann: by the action of phosphorus pentachloride on benzoephenoxy and further treatment with alcohol and soda lye he obtained, surprisingly, benzanilide.

This "Beckmann transposition," as it was baptized by Victor Meyer, played an important part in clearing up the structure of ald- and ketoximes. Meyer obtained in 1872 aliphatic nitrocompounds or nitroparaffins by the action of silver nitrite on alkyl iodides.

The theory of asymmetric carbon atom was transferred to the compounds of quinquivalent nitrogen when Le Bel obtained in 1890 an optically active nitrogen compound by the action of fungi. Similar experiments were made by Edgar Wedekind (born 1870), professor at Hannover-Muenden and Goettingen, Sir William Pope, professor at Manchester and Cambridge. Jakob Meisenheimer professor at Berlin, Greifswald and Tuebingen, and others.

Corresponding compounds of quinquivalent phosphorus, quadrivalent sulfur and trivalent tin



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